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ON THE SULPHO-CINNAMIC ACIDS.

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As is well known, when chlorine, nitric acid, sulphuric acid, etc., act upon aromatic hydrocarbons containing such groups as CH_3, C_2H_5, etc., the principal product is usually a para-compound, while the isomeric ortho-compound is formed at the same time in smaller quantity. If, on the other hand, the carboxyl group is present in the hydrocarbon, the principal product is usually a meta-compound. If a neutral group be interposed between the benzene nucleus and the acid residue, as in the compound $C_6H_5.CH_2.COOH$, the carboxyl group loses the power of determining the position of substituting groups subsequently entering the nucleus. Beilstein and Kuhlberg[1] have shown that phenylacetic acid, $C_6H_5.CH_2.COOH$, conducts itself in the same way towards nitric acid as toluene, for, by nitrating phenylacetic acid, para- and ortho-nitrophenylacetic acids are formed; para- and ortho-nitrophenylpropionic acids are likewise obtained by the action of nitric acid on phenylpropionic acid. These investigations further show that from nitric acid and cinnamic acid, $C_6H_5.CH{=}CH.COOH$, para- and ortho-nitrocinnamic acids are formed.

Rudnew has observed[2] that two sulphocinnamic acids are formed when cinnamic acid is dissolved at the ordinary temperature in

[1] Annalen der Chemie, **163**, 140.

[2] Annalen der Chemie, **173**, 8.

fuming sulphuric acid. The principal product is parasulphocinnamic acid; while the second one, which is formed in very small quantity, is believed by Rudnew to be the meta and not the ortho compound, the formation of which would naturally be expected. This metasulphocinnamic acid was converted, by fusion with potassium hydroxide, into oxybenzoic acid. Rudnew attempted to oxidize it with sulphuric acid and potassium bichromate, but failed to obtain a satisfactory result.

The conduct of the substance towards the chromic acid mixture led to the suspicion that though described by Rudnew as a meta compound, it might possibly prove to be an ortho compound. It seemed probable that, if the two sulphuric acids were converted into the corresponding amides, and then oxidized, it would be an easy matter to recognize even a small quantity of the ortho derivatives, if present. This should be the substance which was discovered and described by Remsen and Fahlberg[1] under the name benzoic sulphinide, $C_6H_4\begin{Bmatrix} CO \\ SO_2 \end{Bmatrix}NH$. It has a very marked sweet taste, and its presence can easily be detected by means of this property. As will be seen, the results reached are not quite satisfactory, though they are rather confirmatory of Rudnew's view than otherwise. In connection with the main work some new derivatives of parasulphaminecinnamic acid have been studied.

Sulpho-Cinnamic Acids.

One sulphocinnamic acid has been known for several years. Marchand obtained it first by treating cinnamic acid with sulphuric acid, and described the barium and lead salts.[2] Herzog subsequently prepared it in a purer condition and added a few salts to Marchand's lists.[3] Rudnew's method for the preparation of the sulphocinnamic acids involves the use of a much smaller quantity of fuming sulphuric acid than had been previously employed. The sulphuric acid which he used contained 20 per cent. of sulphuric anhydride. He also found that the yield of the sulphocinnamic acids is much larger if cinnamic acid be treated with fuming sulphuric acid of this strength, than when a weaker sulphuric acid is employed. The formation of a resinous product is thereby almost entirely avoided, while such a product always attends the use of a

[1] This Journal, **1**, 170. [2] Journal prak. Chemie, **16**, 60. [3] *Ibid.* **29**, 51.

sulphuric acid containing a smaller proportion of anhydride, thus causing considerable loss of material.

The separation of the two sulphocinnamic acids is most easily accomplished by means of their acid barium salts. The acid barium salt of parasulphocinnamic acid crystallizes in long needles which are very difficultly soluble in cold water. The corresponding salt of the isomeric acid is more easily soluble than the para salt. This method Rudnew recommends, and I have adopted it for the preparation and isolation of the sulphocinnamic acids for my experiments.

60 grams of pure and finely powdered cinnamic acid were gradually dissolved in fuming sulphuric acid containing 20 per cent. anhydride. The mixture was kept cool during the operation. Each portion of the cinnamic acid was completely dissolved before the succeeding portion was added. In the act of solution a slight elevation of temperature was observed. When the cinnamic acid was completely dissolved, the liquid was diluted with five or six times its volume of water. The sulphuric acid was neutralized with barium carbonate until barium chloride caused no further precipitate. After the removal of the precipitated barium sulphate, the solution, containing the free sulphonic acids, was divided into two equal portions. One-half was exactly neutralized with a solution of barium hydroxide; the other portion was then added to it. Upon evaporating the solution to a sufficient concentration, the acid para barium salt crystallized out in long needles. A small quantity of the para salt was obtained by further evaporation.

The mother liquor was then evaporated to a small volume, when the meta acid barium salt made its appearance in concretionary aggregates. To remove from the meta salt the para salt, which still adhered to it, it was repeatedly boiled with a small quantity of water, and was thus obtained quite pure. A slight color was removed with animal charcoal.

Parasulphocinnamide.—The barium was exactly precipitated from a hot aqueous solution of the acid para barium sulphocinnamate by means of a solution of potassium carbonate. After the precipitate of barium carbonate was removed, the aqueous solution of the potassium salt was evaporated to dryness. From the dry neutral potassium salt the double amide is obtained by gently heating the salt with phosphorus pentachloride. The acid chloride is a semi-liquid which solidifies on cooling. The chloride by treat-

ment with concentrated aqueous ammonia is converted into the amide. The para double amide is obtained in a pure condition by three or four recrystallizations from hot water. It crystallizes in clusters of needles, which are easily soluble in hot water, but more difficultly soluble in cold water. It fuses at 218° C. (uncorrected). The air-dried amide was analyzed with the following result:

0.1265 gram substance gave 13.9 cc. N at 756 mm. pressure, and 21.5° C. = 0.0156904 gram N.

For $C_9H_{10}O_3SN_2 = C_6H_4 < \begin{matrix} C_2H_3.CONH_2 \\ SO_2NH_2 \end{matrix}$.

	Calculated.		Found.
$C_9H_{10}O_3S$	198	87.61	...
N_2	28	12.39	12.40
	226	100.00	

Oxidation of the para amide.—A small quantity of the pure amide was placed in a flask and treated with the usual oxidizing mixture of sulphuric acid, potassium bichromate and water. The mixture was heated over a small flame, when a violent reaction occurred, and in a few minutes the amide was completely oxidized. Upon diluting the solution with water the product of oxidation crystallized out, and after the solution had become cold it was placed on a filter and thoroughly washed. The product was redissolved in hot water and purified by recrystallization. It is an acid, and crystallizes in flat prisms; it is decomposed at a temperature of about 280° C. without melting. It is very difficultly soluble in cold water, but more easily in hot water. Its properties correspond to the properties which Remsen ascribes to para-sulphamine-benzoic acid, obtained by the oxidation of paratoluene-sulphamide with the chromic acid mixture.

The *barium salt* is very soluble in water, and crystallizes in granular aggregates from the concentrated aqueous solution. An analysis of the air-dried salt was made.

0.2987 gram Ba salt lost 0.0097 gram H_2O at 120° C., and gave 0.1234 gram $BaSO_4$ = 0.07255 gram Ba.

For $(C_7H_6SO_4N)_2Ba + H_2O = \left(C_6H_4 < \begin{matrix} CO_2 \\ SO_2NH_2 \end{matrix}\right)_2 Ba + H_2O$.

	Calculated.		Found.
$C_{14}H_{12}S_2O_8N_2$	400	72.08	...
Ba	137	24.68	24.29
H_2O	18	3.24	3.24
	555	100.00	

Parasulphamine-Cinnamic Acid.

The double amide already described was heated on a water bath with a solution of sodium hydroxide. When the ammonia ceased to be evolved, the solution was neutralized with hydrochloric acid, and filtered to remove any undecomposed amide.

On acidifying the solution with hydrochloric acid a crystalline precipitate was formed, which, redissolved in boiling water, crystallized, as the solution cooled, in long needles. Only one crystallization from hot water was necessary to purify the product.

When dry, it was analyzed.

I. 0.1953 gram substance gave 10.3 cc. N at 753 mm. pressure, and 17° C. = 0.01183385 gram N.

II. 0.1979 gram substance gave 10.8 cc. N at 756.5 mm. pressure, and 18.8° C = 0.01230653 gram N.

For $C_9H_9O_4SN = C_6H_4 < \begin{matrix} C_2H_2.COOH \\ SO_2NH_2 \end{matrix}$.

	Calculated.		Found.	
			I.	II.
$C_9H_9O_4S$	213	93.83	...	...
N	14	6.17	6.06	6.22
	227	100.00		

The substance possesses the properties of an acid. At 21° C. 0.058 parts are soluble in 100 parts of water. It is difficultly soluble even in hot water. From a hot aqueous solution it crystallizes in long thick needles. Alcohol dissolves it quite readily, and ether with difficulty. At 250° C. it decomposes without melting.

Barium salt.—This salt is obtained by boiling parasulphamine-cinnamic acid with an excess of barium carbonate. From the filtered solution the salt crystallizes in thick needles. It is soluble in cold water, and very easily soluble in hot water.

The air-dried salt was analyzed.

I. 0.26 gram Ba salt lost 0.0149 gram H_2O at 120° C., and gave 0.0966 gram $BaSO_4$ = 0.05679 gram Ba.

II. 0.235 gram Ba salt lost 0.0135 gram H_2O at 120° C., and gave 0.0875 gram $BaSO_4$ = 0.05144 gram Ba.

For $(C_9H_8SO_4N)_2Ba + 2H_2O$.

	Calculated.		Found.	
			I.	II.
$(C_9H_8SO_4N)_2$	452	72.32	...	...
Ba	137	21.92	21.84	21.88
$2H_2O$	36	5.76	5.73	5.74

Calcium salt.—The calcium salt is obtained by treating a boiling solution of parasulphamine-cinnamic acid with finely powdered Iceland spar. The salt crystallizes in clusters of fine needles, which are not very difficultly soluble in water.

Analyses of the air-dried salt were made.

I. 0.3934 gram Ca salt lost 0.0141 gram H_2O at 120° C., and gave 0.1053 gram $CaSO_4$ = 0.03097 gram Ca.

II. 0.3864 gram Ca salt lost 0.0139 gram H_2O at 120° C., and gave 0.1033 gram $CaSO_4$ = 0.03038 gram Ca.

For $(C_9H_8SO_4N)_2Ca + H_2O$.

	Calculated.		Found.	
			I.	II.
$(C_9H_8SO_4N)_2$	452	88.64	...	...
Ca	40	7.84	7.87	7.86
H_2O	18	3.52	3.58	3.59
	510	100.00		

Oxidation of Parasulphamine-Cinnamic Acid.

It has already been stated that by heating the para double amide with a solution of caustic soda, ammonia is evolved and an acid containing but one nitrogen atom is formed.

9 grams of this acid were placed in a balloon flask with 20 grams of potassium bichromate and 30 grams of concentrated sulphuric acid, diluted with three times its volume of water. The mixture was heated for four or five hours. At the end of this time it was diluted with water, and, after it had cooled, the insoluble product which had crystallized out was placed on a filter

and thoroughly washed. It was redissolved in hot water, from which it crystallized out in flat plates as the solution cooled. After two or three crystallizations the product was obtained colorless and perfectly pure.

It is very difficultly soluble even in hot water, and is decomposed at 280° C. without fusing. The barium salt is very soluble in water, but crystallizes from a concentrated solution. The salt, dried in the air at the ordinary temperature, was analyzed with the following result:

I. 0.3385 gram Ba salt lost 0.0107 gram H_2O at 120° C., and gave 0.1426 gram $BaSO_4 = 0.0838$ gram Ba.

II. 0.2864 gram Ba salt lost 0.0088 gram H_2O at 120° C., and gave 0.1221 gram $BaSO_4 = 0.0717$ gram Ba.

For $(C_7H_6SO_4N)_2Ba + H_2 = \left(C_6H_4\langle^{COO}_{SO_2NH_2}\right)Ba + H_2O$.

	Calculated.		Found.	
			I.	II.
$(C_7H_6SO_4N)_2$	400	72.08	...	...
Ba	137	24.68	24.75	25.03
H_2O	18	3.24	3.16	3.07
	555	100.00		

The acid just described is identical with the acid obtained by oxidizing the para double amide of cinnamic acid, and possesses all the properties of para-sulphamine-benzoic acid, obtained by oxidizing paratoluene-sulphamide with the chromic acid mixture.[1]

The acid formed by the action of caustic soda on the para double amide of cinnamic acid is therefore $C_6H_4\langle^{C_2H_2COOH}_{SO_2NH_2}$, as we would expect, and the name para-sulphamine-cinnamic acid describes its constitution.

Metasulpho-Cinnamic Acid.

When the para acid barium salt had been entirely removed from the meta acid barium sulphonate, the aqueous solution of the latter was treated with a solution of potassium carbonate in sufficient quantity to exactly precipitate the barium. The solution was filtered from the precipitated barium carbonate and evaporated to

[1] Annalen der Chemie, **178**, 297 ff.

dryness. The perfectly dry meta potassium salt (five parts) was treated with phosphorus pentachloride (seven parts), the mixture being kept cool during the operation. When the action of the pentachloride upon the salt had ended, concentrated aqueous ammonia was added in excess. On standing several hours the amide crystallized out. It is more easily soluble in cold water than the corresponding para amide. As the quantity of the meta amide in my possession was small, it was very difficult to obtain it perfectly pure.

Oxidation of the meta amide.—Since Rudnew was unable to obtain a satisfactory result by oxidizing meta-sulpho-cinnamic acid with the chromic acid mixture, I subjected the double amide to the oxidizing action of potassium permanganate, hoping thereby to obtain an easily recognizable product.

The following proportions were taken: 5 grams of the amide, 20 grams of potassium permanganate, and 200 cc. water, made distinctly alkaline with a small quantity of caustic soda solution.

The mixture was heated for eight hours on a water-bath; reduction of the permanganate occurred with evolution of ammonia. When the ammonia had ceased to be evolved, the reduction of the permanganate was completed by means of sulphurous acid, and the solution, filtered from the manganese oxides, was evaporated to a small volume. It was then acidified, and as no precipitate was formed, the solution was evaporated to dryness, and the dry mass repeatedly treated with alcohol. Upon evaporating the alcoholic solution to dryness, an organic residue was left, which is readily soluble in water. It possesses no distinctly sweet taste, and its other properties differ materially from the properties of benzoic sulphinide, which Remsen and Fahlberg obtained by oxidizing orthotoluene sulphamide in a similar manner. As far as could be judged from the experiments performed, not a trace of benzoic sulphinide was formed in the oxidation of metasulphocinnamide with potassium permanganate. Further, a small quantity of the meta amide was fused with potassium hydroxide, but I was unable to detect the presence of salicylic acid in the product.

If these results, although in themselves of a negative character, be taken in connection with Rudnew's positive results, namely, that by fusion with potassium hydroxide the sulphocinnamic acid yields oxybenzoic acid, the proof is sufficiently strong to justify the conclusion that the sulphocinnamic acid, which is formed in

small quantity by the action of sulphuric acid on cinnamic acid, is not orthosulphocinnamic acid. It may, however, be regarded as an open question whether Rudnew's acid was really metasulphocinnamic acid. The conduct of the substance towards chromic acid seems particularly to justify this, as it has been shown[1] that meta compounds conduct themselves like para compounds, easily yielding oxidation products, while this so-called meta acid breaks up when oxidized. The small quantity of the acid formed prevented a more complete study.

The work described in this paper was undertaken at Professor Remsen's suggestion, and was conducted in the chemical laboratory, under his supervision and with his assistance.

April, 1882.

Contributions from the Chemical Laboratory of Harvard College.

XXI.—DIBROMACRYLIC ACID.[2]

By Henry B. Hill.

In a communication upon furfurol and certain of its derivatives which I laid before the American Academy of Arts and Sciences a year ago, I described a dibromacrylic acid[3] which O. R. Jackson and I had some time before obtained from mucobromic acid by the action of alkalies. Although we had not been able to prepare the acid in a state of perfect purity, still our results seemed to us sufficient for its identification; and since it then appeared that a more extended study of it would interfere with other investigators in the same field, further work upon it had been for the time given up. Not long afterward it became evident that our hesitation upon this account had been quite unnecessary; but it was not until recently that I was able to take up again the study of this acid. I have now obtained results which correct our previous observations in several important particulars.

[1] This Journal, **3**, 142.

[2] Proceedings Amer. Academy. Communicated by the Author.

[3] This Journal, **3**, 106; and Proceedings Amer. Academy, **16** (N. S. viii), 192.

For the preparation of the acid, O. R. Jackson and I used chiefly the barium salt, which crystallized well from water or dilute alcohol, and which gave us constant analytical results. The air-dried salt lost nothing *in vacuo* over sulphuric acid, or when heated to 80°, and the percentage of barium which it contained agreed closely with that required by the formula $Ba(C_3HBr_2O_2)_2$. We therefore with little hesitation considered the salt anhydrous, and were inclined to ascribe the slight loss of weight which we noticed at 100° to a slow decomposition. The acid made from carefully prepared barium salt crystallized well, melted quite sharply at 83–84°, but on analysis proved to contain too high a percentage of bromine. Since the acid made from the lead salt had given us precisely the same unsatisfactory results, we thought it probable that the impurities which were found in the acid thus made were introduced by a decomposition of the acid itself in its liberation from its salts. A more careful study of this reaction subsequently convinced me, however, that such was not the case. Certainly no carbonic dioxide, bromacetylen, or hydrobromic acid could be detected as resulting from such decomposition when dilute sulphuric acid was added in slight excess to a boiling aqueous solution of the barium salt. I therefore turned my attention to a further purification of the salts.

Since repeated recrystallization of the barium salt failed to give me any much better product, I thought it worth while to determine the variation of composition introduced by one set of crystallizations from water. I therefore dissolved 30 grams of white well crystallized salt (A) in 380 cc. of hot water. On cooling, 6.5 grams of the salt (I) separated, and by successive filtration, evaporation, and cooling, I obtained the fractions (II) 8.9 grams, (III) 6.9 grams, and (IV) 4.8 grams, the remaining 2.9 grams being lost in the filter-papers upon which the successive portions were dried. An analysis of these air-dried salts gave the following results:

A. 0.5669 gram substance gave 0.2239 gram $BaSO_4$.
I. 0.5713 gram substance gave 0.2276 gram $BaSO_4$.
II. 0.5139 gram substance gave 0.2036 gram $BaSO_4$.
III. 0.5665 gram substance gave 0.2231 gram $BaSO_4$.
IV. 0.5003 gram substance gave 0.1941 gram $BaSO_4$.

	Calculated for $Ba(C_3HBr_2O_2)_2$.	Calculated for $Ba(C_3HBr_2O_2)_2.H_2O$.	Found.				
			A.	I.	II.	III.	IV.
Ba	23.03	22.35	23.21	23.43	23.29	23.15	22.80

From these results it was evident that the barium salt contained a persistent impurity which could not be removed by fractional crystallization, and that the constancy of its composition was accidental. I next tried the beautifully crystalline acid potash salt which I have already described,[1] and found that it gave results which were all that could be desired. This salt can easily be made by neutralizing a weighed amount of the ordinary acid melting at 82–84° with potassic carbonate, and adding to the hot solution an equal amount of the acid dissolved in a little hot water. As the solution cools the salt separates in long silky needles, which after a few recrystallizations from hot water yield an acid whose melting point is constant. The loss in recrystallization is comparatively small, since the salt is but sparingly soluble in cold water and dissolves very freely in hot. The analyses which I have made of the acid prepared in this way show its perfect purity.

I. 0.2183 gram substance gave by the method of Carius 0.3573 gram AgBr.

II. 0.2127 gram substance gave 0.3476 gram AgBr.

III. 0.2530 gram substance gave 0.4137 gram AgBr.

	Calculated for $C_3H_2Br_2O_2$.	Found.		
		I.	II.	III.
Br	69.56	69.66	69.56	69.60

The pure acid melts at 85.5–86°, but in other respects does not differ essentially in its physical properties from the product which I have already described. The solubility of the acid was determined by neutralizing with baric carbonate an aqueous solution of the acid prepared according to the method of V. Meyer, and precipitating with sulphuric acid the barium dissolved.

I. 12.7854 grams of a solution saturated at 17.5° gave 0.3107 gram $BaSO_4$.

II. 13.5723 grams of a solution saturated at 17.5° gave 0.3303 gram $BaSO_4$.

III. 10.8488 grams of a solution saturated at 18° gave 0.2695 gram $BaSO_4$.

IV. 9.7341 grams of a solution saturated at 18° gave 0.2434 gram $BaSO_4$.

According to these determinations, the aqueous solution saturated at 17.5° and 18° contains the following percentages:

[1] *Loc. cit.* p. 194.

I.	17.5°. II.	III.	18°. IV.
4.80	4.81	4.90	4.94

Baric Dibromacrylate, $Ba(C_3HBr_2O_2)_2.H_2O$.—The barium salt prepared by neutralizing a solution of the pure acid with baric carbonate did not differ in outward appearance from the salt made directly from mucobromic acid by the action of baric hydrate, but proved on analysis to contain a percentage of barium materially lower than that which O. R. Jackson and I had previously obtained, and closely agreeing with that required by one molecule of water of crystallization. When dried by exposure to the air the salt lost nothing over sulphuric acid or when heated to 85°, but by long continued heat at 100° (75 to 100 hours), or more rapidly at 120°, it gave up its crystal water without showing any signs of decomposition.

I. 0.6642 gram of the air-dried salt gave by precipitation 0.2540 gram $BaSO_4$.

II. 0.6392 gram of the air-dried salt gave on ignition with H_2SO_4 0.2434 gram $BaSO_4$.

III. 0.5300 gram of the air-dried salt lost at 120° 0.0161 gram H_2O.

IV. 1.9253 gram of the air-dried salt lost at 100° 0.0548 gram H_2O.

V. 1.1582 gram of the air-dried salt lost at 100° 0.0351 gram H_2O, and gave by precipitation with H_2SO_4 0.4408 gram $BaSO_4$.

Calculated for $Ba(C_3HBr_2O_2)_2.H_2O$.		Found.				
		I.	II.	III.	IV.	V.
Ba	22.35	22.48	22.39	...	...	22.28
H_2O	2.94	...	...	3.04	2.85	3.03

The solubility of the salt was also determined.

I. 9.4276 grams of an aqueous solution saturated at 18° gave by precipitation 0.2214 gram $BaSO_4$.

II. 8.4088 grams of a solution saturated at 18° gave 0.1917 gram $BaSO_4$.

According to these determinations the aqueous solution of the salt saturated at 18° contains the following percentages of the anhydrous salt:

I.	II.
6.00	5.82

Plumbic Dibromacrylate, $Pb(C_3HBr_2O_2)_2.H_2O$.—The lead salt which, according to the analyses made of former preparations, was anhydrous when made from the pure acid by neutralization with plumbic carbonate, or from the acid potassium salt by precipitation with plumbic acetate, likewise proved to contain one molecule of water of crystallization.

I. 0.5972 gram of the air-dried salt lost at 100° 0.0161 gram H_2O, and gave by ignition with H_2SO_4 0.2655 gram $PbSO_4$.

II. 1.0438 gram substance dried over H_2SO_4 lost at 100° 0.0283 gram H_2O, and gave by ignition with H_2SO_4 0.4622 gram $PbSO_4$.

	Calculated for $Pb(C_3HBr_2O_2)_2.H_2O$.	Found. I.	II.
Pb	30.31	30.37	30.25
H_2O	2.64	2.70	2.71

Calcic Dibromacrylate, $Ca(C_3HBr_2O_2)_2.3H_2O$.—The calcium salt made from the pure acid crystallized in long clustered needles, which gave on analysis results identical with those which O. R. Jackson and I formerly obtained.

I. 2.1502 grams of the air-dried salt lost at 80–85° 0.2034 gram H_2O.

II. 1.2264 gram of the air-dried salt lost at 95–100° 0.1171 gram H_2O.

III. 1.8124 gram of the air-dried salt lost at 100° 0.1755 gram H_2O.

	Calculated for $Ca(C_3HBr_2O_2)_2.3H_2O$.	Found. I.	II.	III.
H_2O	9.78	9.46	9.55	9.68

I. 0.4393 gram of the salt dried at 100° gave on ignition with H_2SO_4 0.1199 gram $CaSO_4$.

II. 0.6161 gram of the salt dried at 100° gave on ignition with H_2SO_4 0.1674 gram $CaSO_4$.

	Calculated for $Ca(C_3HBr_2O_2)_2$.	Found. I.	II.
Ca	8.03	8.03	7.99

Potassic Dibromacrylate, $KC_3HBr_2O_2$.—The analysis of the potassium salt made by neutralizing the pure acid with potassic carbonate showed that it was anhydrous, as it had previously been described.

I. 0.7334 gram of the salt dried over H_2SO_4 gave on ignition with H_2SO_4 0.2373 gram K_2SO_4.

II. 0.7507 gram of the salt dried over H_2SO_4 gave 0.2427 gram K_2SO_4.

	Calculated for $KC_3HBr_2O_2$.	Found.	
		I.	II.
K	14.58	14.53	14.51

Although many unsuccessful attempts had previously been made to prepare brompropiolic acid in a pure state, it seemed to me not impossible that the prolonged action of alkalies in the cold might remove from the dibromacrylic acid a molecule of hydrobromic acid, and that a purer product might thus be obtained. I found, however, that the reaction was extremely slow, at least with baric hydrate. An aqueous solution which contained one molecule of baric hydrate to each molecule of dibromacrylic acid was strongly alkaline even after standing for fifteen days, and gave on acidification and extraction with ether the compound of brompropiolic and dibromacrylic acids which has already been described. After recrystallization from ligroin the substance melted at 103°, and gave on analysis the following result:

0.2535 gram substance gave 0.3766 gram AgBr.

	Calculated for $C_6H_3Br_3O_4$.	Found.
Br	63.33	63.22

Since I had before noticed that this intermediate product could be obtained from dibromacrylic acid by the action of baric hydrate in the course of a few hours, and that malonic acid was formed even in the cold after the lapse of several months, it was evident that further attempts in this direction were useless.

XXII.—ON THE CRYSTALLINE FORM OF α-DICHLORACRYLIC ACID.

By W. H. Melville.

(Communicated by H. B. Hill.)

Although the physical properties of the β-dichloracrylic acid of Wallach[1] are decidedly different from those which W. Z. Bennett and I found to be characteristic of the dichloracrylic acid made

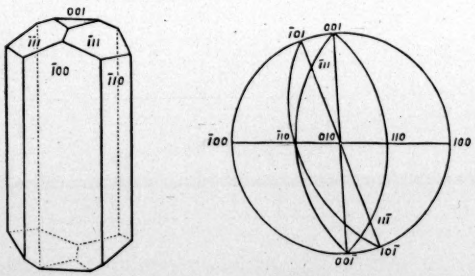
[1] Annalen der Chemie, **93**, 19.

from mucochloric acid,[1] a difference which appeared to be fully confirmed by a comparison of the salts of the two acids, still it seemed to me desirable to prove with a little more precision the difference between the two. Since Wallach had made no determinations of the solubility of his acid or its salts, and moreover thought[2] that little weight should be attached to the determinations of crystal-water which he had as yet published, there remained no definite, well-established points of difference except the melting points (86° and 77°) and a difference in the crystalline form of the potassium salt: one crystallizing in needles, the other in hexagonal plates. Since the β acid had been obtained in measurable crystals and fully described in Wallach's first paper, although we had previously been unable to get measurable crystals of our acid, I made fresh attempts with larger quantities of material than had then been at our disposal. I found that by the slow cooling of a warm, moderately dilute solution in chloroform, well-developed crystals could be obtained, although the determination of the crystals was rendered difficult on account of the rapid roughening of their faces when exposed to the air. Dr. W. H. Melville succeeded, however, in making the necessary measurements, and to his kindness I am indebted for the following description. The purity of the material used was determined by analysis.

0.2061 gram of the substance gave 0.4198 gram AgCl.

	Calculated for $C_3H_2Cl_2O_2$.	Found.
Cl	50.36	50.35

CRYSTALLINE FORM OF DICHLORACRYLIC ACID.



[1] This Journal, **3**, 167; and Proceedings Amer. Academy, **16**, 206.
[2] Ann. Chem. u. Pharm. **203**, 83.

Monoclinic System.

Forms, [100] [001] [110] [$\bar{1}$11].

Elements: Clinodiagonal a=1.1865
Orthodiagonal b=1
Vertical Axis c=0.3637
Angle of Axes XZ=87° 32′

Angles between Normals.

	Observed.	Calculated.
111 and 111	=37° 54′	Fundamental angles.
$\bar{1}$11 " 001	=25° 8′	Fundamental angles.
$\bar{1}$11 " $\bar{1}$00	=71° 49′	Fundamental angles.
001 " 100	=87° 32′	87° 33′
$\bar{1}$00 " $\bar{1}$10	=49° 56′	49° 51′
110 " 110	=80° 6′	80° 18′

Although Wallach's dichloracrylic acid also crystallizes in the monoclinic system, the forms are totally unlike, and the difference between the two acids is therefore established.

XXIII.—ON THE RELATIONS BETWEEN DIBROMACRYLIC ACID AND TRIBROMPROPIONIC ACIDS.

By Henry B. Hill and Clement W. Andrews.

Nearly two years ago Michael and Norton[1] published a description of the tribrompropionic acid melting at 92° which was first mentioned by Linneman and Penl,[2] and which they obtained by the addition of bromine to the so-called β-monobromacrylic acid of Tollens and Wagner. In this paper they remarked that potassic hydrate attacked the acid readily in alcoholic solution, but they attempted no isolation of the dibromacrylic acid which was thus formed. They soon afterwards offered to relinquish the farther study of this acid, in case we felt interested to undertake its preparation and comparison with the dibromacrylic acid which one of us had already described. This kind offer was accepted, and we began the investigation at once. Although we had no difficulty in

[1] This Journal, **2**, 18. [2] Berichte der deutsch. chem. Gesellsch. **8**, 1098.

the isolation of a dibromacrylic acid which closely resembled that which had been made from mucobromic acid, still it was impossible to establish the identity of the two until the latter had been somewhat more carefully studied. In the meantime Mauthner and Suida,[1] in an article upon substituted acrylic and propionic acids, described again the preparation of the tribrompropionic acid melting at 92°, without having seen more than a brief notice of Michael and Norton's work. In this article they further showed that it might be converted by the action of potassic hydrate into a dibromacrylic acid, which, as they asserted, was identical with that which O. R. Jackson and one of us had obtained from mucobromic acid.[2] The only facts which they brought forward in support of this assertion were, the melting-point, 85°, the ready formation of malonic acid by the action of baric hydrate, and the anhydrous form of the lead salt. Since neither the melting-point nor the action of baric hydrate will discriminate between the two isomeric forms of dibromacrylic acid already known, and, moreover, since the lead salt of one of these two acids has never been described and of the other is not anhydrous, as one of us has recently shown, it is evident that these facts were wholly insufficient to characterize the acid in question. Our investigation of the same acid has shown us that their assertion, though unsupported by evidence, was accidentally correct.

Dibromacrylic Acid, $C_3H_2Br_2O_2$.—In the preparation of the tribrompropionic acid necessary for this research we followed quite closely the method of Michael and Norton, although we did not consider it necessary to purify the dibrompropyl alcohol by distillation under diminished pressure before oxidation. For the conversion of the tribrompropionic acid into the corresponding dibromacrylic acid we have found it most advantageous to dissolve it in the calculated amount of a titrated solution of baric hydrate, and to allow the reaction to proceed at ordinary temperatures. After standing for several days the neutral or at most feebly alkaline solution was evaporated, and the acid extracted from the recrystallized barium salt thus obtained. Since this acid was found by preliminary trial to give a sparingly soluble acid potassium salt which crystallized in long silky needles, for further purification it was converted into this salt. After several recrystallizations from hot water, the acid was set free by the addition of hydrochloric

[1] Sitzungsberichte der kk. Akademie, Wien, **83**, 273.
[2] This Journal, **3**, 106; and Proceedings Amer. Acad. **16**, 192.

acid and extracted with ether. The acid thus obtained crystallized in small oblique prisms readily soluble in alcohol, ether, and chloroform, more sparingly in benzol or carbonic disulphide. Under water the crystals melted at about 20° to a colorless oil which dissolved readily on heating. The acid dried over sulphuric acid melted at 85–86°, and gave on analysis percentages corresponding to the formula $C_3H_2Br_2O_2$.

I. 0.7497 gram substance gave on combustion 0.4341 gram CO_2 and 0.0673 gram H_2O.

II. 0.2863 gram substance gave 0.4691 gram AgBr.

III. 0.2093 gram substance gave 0.3432 gram AgBr.

Calculated for $C_3H_2Br_2O_2$.		Found.		
		I.	II.	III.
C	15.65	15.79	...	...
H	0.87	1.00	...	...
Br	69.56	...	69.72	69.84

The solubility of the acid we determined by neutralizing with baric carbonate an aqueous solution prepared according to the method of V. Meyer and determining by precipitation the barium dissolved.

I. 12.4640 grams of a solution saturated at 18° gave 0.3124 gram $BaSO_4$.

II. 12.2745 grams of a solution saturated at 18° gave 0.3091 gram $BaSO_4$.

According to these determinations the aqueous solution saturated at 18° contained the following percentages:

I.	II.
4.95	4.97

Baric Dibromacrylate, $Ba(C_3HBr_2O_2)_2.H_2O$.—The barium salt made by neutralizing a solution of the acid with baric carbonate crystallized in rhombic plates more or less irregular in form, which, when dried by exposure to the air, contained one molecule of water.

I. 1.3641 gram of salt dried over H_2SO_4 gave by precipitation 0.5195 gram $BaSO_4$.

II. 3.1482 grams of the air-dried salt lost at 110° 0.0933 gram H_2O; 0.8202 gram of the same air-dried salt gave by precipitation 0.3147 gram $BaSO_4$.

III. 1.7219 gram of salt dried over H_2SO_4 lost at 120° 0.0520 gram H_2O; 0.6769 of the same salt gave by precipitation 0.2555 gram $BaSO_4$.

Calculated for $Ba(C_3HBr_2O_2)_2.H_2O$.		Found.		
		I.	II.	III.
Ba	22.35	22.40	22.56	22.19
H_2O	2.94	...	2.96	3.02

For its further identification we determined its solubility in water at 18°.

9.2373 grams of a solution saturated at 18° gave by precipitation 0.2131 gram $BaSO_4$.

From this determination it follows that the aqueous solution saturated at 18° contained 5.89 per cent. of the anhydrous salt.

Calcic Dibromacrylate, $Ca(C_3HBr_2O_2)_2.3H_2O$.—The calcium salt crystallized in clustered needles which contained three molecules of water of crystallization when dried by exposure to the air.

I. 0.5761 gram of the air-dried salt lost at 80° 0.0535 gram H_2O.

II. 0.5101 gram of the air-dried salt lost at 80° 0.0491 gram H_2O.

Calculated for $Ca(C_3HBr_2O_2)_2.3H_2O$.		Found.	
		I.	II.
H_2O	9.78	9.29	9.63

0.4608 gram of the salt dried at 80° gave on ignition with H_2SO_4 0.1262 gram $CaSO_4$.

	Calculated for $Ca(C_3HBr_2O_2)_2$.	Found.
Ca	8.03	8.06

Potassic Dibromacrylate, $KC_3HBr_2O_2$.—The potassium salt was made from the acid by neutralization with potassic carbonate. It crystallized in leafy plates which were anhydrous.

0.6842 gram of the air-dried salt gave on evaporation with H_2SO_4 and ignition 0.2229 gram K_2SO_4.

	Calculated for $KC_3HBr_2O_2$.	Found.
K	14.58	14.62

A comparison of these results with those which one of us has presented in the preceding paper will be facilitated by the following table, which gives the mean of each series of results:

	Dibromacrylic Acid from	
	Mucobromic	Tribrompropionic
Melting point, ...	85.5–86°	85–86°
Aqueous solution 18°, per cent. acid, .	4 92	4.96
Barium salt, per cent. water, . . .	2.97	2.99
Barium salt solubility 18°, ...	5.91	5.89
Calcium salt, per cent. water, . . .	9.56	9.46

Since the identity of the dibromacrylic acid formed by the subtraction of hydrobromic acid from the tribrompropionic acid melting at 92° with that derived from mucobromic acid was thus established with precision, it seemed to us of interest to study a little more closely the tribrompropionic acid which this same dibromacrylic acid forms by the addition of hydrobromic acid. Mr. C. F. Mabery[1] had with one of us already proved that such an addition product could be formed, but it had been prepared solely from the impure acid melting at 83–84° and very little studied. We therefore at first undertook its preparation in larger quantity from pure acid melting at 85–86°.

Tribrompropionic Acid, $C_3H_3Br_3O_2$.—When dibromacrylic acid made by the action of baric hydrate upon mucobromic acid is heated with three or four times its weight of hydrobromic acid saturated at 0° for eight or ten hours at 100° the needle-like prisms disappear and are replaced by rectangular plates of the new tribrompropionic acid. With the pure acid no carbonization such as had been noticed in working with the impure acid was observed even at 120°, and we therefore usually allowed the addition to proceed at this higher temperature, since the reaction was then completed in a shorter time. The tubes opened without marked pressure, and the crystalline product, separated from the acid mother-liquors by filtration upon a perforated platinum cone, was dried upon porous tiles. When treated in this way the dibromacrylic acid gave about its own weight of crude tribrompropionic acid. The acid can readily be purified by recrystallizing it successively from ligroin and carbonic disulphide. The use of carbonic disulphide causes considerable loss, but with ligroin alone we failed to obtain as high a melting-point. After several recrystallizations the acid showed a constant melting-point, and gave on analysis the required percentages.

I. 1.0329 gram substance dried over H_2SO_4 gave on combustion 0.4446 gram CO_2 and 0.0994 gram H_2O.

II. 0.2184 gram substance gave 0.3963 gram AgBr.

III. 0.1938 gram substance gave 0.3525 gram AgBr.

	Calculated for $C_3H_3Br_3O_2$.	Found.		
		I.	II.	III.
C	11.57	11.74	...	...
H	0.96	1.07	...	...
Br	77.17	...	77.29	77.39

[1] This Journal, **3**, 116; and Proceedings Amer. Acad. **16**, 197.

This tribrompropionic acid is very soluble in alcohol or ether, somewhat less soluble in chloroform, carbonic disulphide, benzol, or ligroin. It dissolves freely in hot water, but is quite rapidly decomposed on boiling with the formation of hydrobromic acid. From the hot aqueous solution the acid crystallizes on cooling in pearly scales. Repeatedly recrystallized from carbonic disulphide, the acid melts at 118°.

Argentic Tribrompropionate, $AgC_3H_2Br_3O_2$.—Argentic nitrate added to a cold aqueous solution of the acid precipitates the silver salt in small clustered rhombic plates. On warming it with water argentic bromide is rapidly formed, but it may be dried over sulphuric acid without essential decomposition.

0.2901 gram of the salt dried over H_2SO_4 gave by precipitation with HBr 0.1316 gram AgBr.

	Calculated for $AgC_3H_2Br_3O_2$.	Found.
Ag	25.83	26.05

The barium and calcium salts were readily soluble in water, and their solution could not be warmed without the instantaneous formation of bromide. Even on evaporating their solutions at ordinary temperatures over sulphuric acid *in vacuo* the barium salt was almost wholly decomposed; the calcium salt was apparently somewhat more stable, for it was thus obtained in dendritic needles, although the mother-liquor contained calcic bromide. Since the air-dried salt lost nothing over sulphuric acid and was decomposed by heat, the water of crystallization could not be directly determined. It gave, however, a percentage of calcium agreeing closely with that required by two molecules of water.

I. 1.1087 gram of the air-dried salt gave on ignition with H_2SO_4 0.2179 gram $CaSO_4$.

II. 0.7279 gram of the air-dried salt gave on ignition with H_2SO_4 0.1425 gram $CaSO_4$.

	Calculated for $Ca(C_3H_2Br_3O_2)_2.2H_2O$.	Found.	
		I.	II.
Ca	5.75	5.78	5.76

We were unable to prepare other salts.

Dibromacrylic Acid.—The ready decomposition of the tribrompropionic acid made it seem desirable to isolate and identify the dibromacrylic acid which was thus formed. For this purpose we

dissolved pure tribromproprionic acid, melting at 118°, in water, and added from a burette a titrated solution of baric hydrate. So rapid was the action that an alkaline reaction could not be maintained until nearly one molecule of baric hydrate had been added for each molecule of the acid. When the calculated amount of baric hydrate had been added the solution was allowed to stand for half an hour, and then but a trace of baric carbonate could be precipitated with carbonic dioxide. Ether extracted from the acidified solution a crystalline acid melting at 85–86°, which gave on analysis the percentage of bromine required by the formula $C_3H_2Br_2O_2$.

0.1979 gram substance gave 0.3240 gram AgBr.

	Calculated for $C_3H_2Br_2O_2$.	Found.
Br	69.57	69.66

The solubility of the acid in cold water was determined by the method of V. Meyer.

I. 10.7793 grams of a solution saturated at 18° gave on neutralization with baric carbonate and precipitation 0.2908 gram $BaSO_4$.

II. 7.7354 grams of a solution saturated at 18° gave 0.1940 gram $BaSO_4$.

According to these determinations the aqueous solution of the acid saturated at 18° contained the percentages:

I.	II.
5.32	4.95

Baric Dibromacrylate, $Ba(C_3HBr_2O_2)_2.H_2O$.—By neutralizing the acid with baric carbonate, or more conveniently by the direct evaporation of the solution obtained by the action of baric hydrate upon tribromopropionic acid, we obtained the barium salt in leafy rhombic plates which, when dried over sulphuric acid, contained one molecule of water.

I. 1.1489 gram of the salt dried over H_2SO_4 lost at 100-105° 0.0335 gram H_2O.

II. 1.5158 gram of the salt dried over H_2SO_4 lost at 105-110° 0.0457 gram H_2O, and gave on precipitation 0.5790 gram $BaSO_4$.

	Calculated for $Ba(C_3HBr_2O_2)_2.H_2O$.	Found.	
		I.	II.
Ba	22.35	...	22.46
H_2O	2.94	2.92	3.02

Calcic Dibromacrylate, $Ca(C_3HBr_2O_2)_2.3H_2O$.—The calcium salt crystallized in radiating needles which contained when air-dried three molecules of water.

0.9444 gram of the air-dried salt lost at 100–105° 0.0906 gram H_2O, and gave on ignition with H_2SO_4 0.2332 gram $CaSO_4$.

	Calculated for $Ca(C_3HBr_2O_2)_2.3H_2O$.	Found.
Ca	7.25	7.26
H_2O	9.78	9.59

These results are sufficient to prove that this dibromacrylic acid is identical with the one already studied, as a comparison of the mean results given in the following table will show:

	Dibromacrylic Acid from Mucobromic	Tribrompropionic
Melting point, ...	85.5–86°	85–86°
Aqueous solution saturated at 18°, per cent. acid,	4.92	5.12
Barium salt, per cent. water, ...	2.97	2.97
Calcium salt, per cent water, ...	9.56	9.56

ON THE DETERMINATION OF SO-CALLED REVERTED PHOSPHORIC ACID.

By Clifford Richardson.

The usual method for the determination of reverted phosphoric acid depends upon the solubility of dicalcic phosphate and insolubility of tricalcic phosphate in a solution of neutral citrate of ammonia of a specific gravity of 1.09. With the introduction of superphosphates made from mineral sources great dissatisfaction has arisen with this method on the part of the manufacturers, who claim that the oxalate method, which was condemned by Fresenius, is the only one suited to their class of fertilizers.

The minerals, Navassa phosphate, South Carolina rock, &c., from which these superphosphates are manufactured, contain considerable amounts of iron, which causes a speedy reversion

of the phosphoric acid which has been made soluble by sulphuric acid; but in this form, although considered by the producers as "reverted phosphoric acid," and as such possessed of a high commercial value, it is not apparently sufficiently soluble in citrate, employed in the usual manner, to be given as such in the results of the analyses. On this account the use of the oxalate method is demanded.

With a view of showing the varying action of oxalate of ammonia on this class of phosphates, both in their natural and manufactured conditions, the following determinations have been made nearly according to a scheme proposed by a committee appointed at the convention of agricultural chemists in Cincinnati in 1881.

The Varying Action of Oxalate.

Wt. of sub. taken.	Wt. of Oxal. taken.	Volume of solut.	Time of digest.	Temp. of digest.	Precip. Phos. 25.		Navassa Acid, 19.		Navassa Acid, 39.		Navassa raw, 38.		So. Ca. Acid, 41.		So. Ca. raw, 40.		
						P_2O_5, undis.		P_2O_5, undis.		P_2O_5, undis.		P_2O_5, undis.		P_2O_5, undis.			P_2O_5, undis.
Total P_2O_5.					45.50	..	15.75	..	16.18	..	29.64	..	18.61	..	26.47	..	..
Soluble P_2O_5.					..	..	1.30	..	4.47	..	..	..	11.09	..	.	..	..
P_2O_5 Insol. in citrate.					..	..	6.50	..	6.25	..	..	..	5.90	..	..	..	..
Concentration of solution:																	
2.	5.	100.	60′	100°	..	..	..	4.35	3.05	3.37	..	24.78	..	3.59	..	..	22.30
2.	4.	100.	60′	100°	..	21.33	..	8.69	..	6.17	..	25.57	..	4.17	..	24.51	24.06
2.	2.	100.	60′	100°	..	27.88	..	10.63	..	7.94	..	27.18	..	5.69	..	..	24.64
2.	1.	100.	60′	100°	..	34.16	..	12.13	..	9.59	..	28.43	..	6.52	..	..	25.07
Ratio of solution to substance:																	
2.	2.	200.	60′	100°	..	..	..	..	..	7.54	..	26.57	..	5.77	..	..	24.39
2.	2.	100.	60′	100°	..	..	..	..	..	7.97	..	27.53	..	6.07	..	..	24.65
2.	2.	50.	60′	100°	..	..	..	..	..	8.84	..	28.00	..	7.35	..	..	24.74
Time of digestion:																	
2.	2.	100.	120′	100°	..	..	..	..	..	8.01	..	26.54	..	5.27	..	..	24.00
2.	2.	100.	60′	100°	..	..	..	..	..	..	..	27.09	..	5.98	..	..	24.37
2.	2.	100.	30′	100°	..	..	..	..	..	9.67	..	27.99	..	6.36	..	..	24.59
Temperature of digestion:																	
2.	2.	100.	60′	100°	..	..	..	4.35	..	7.88	..	27.18	..	5.84	..	..	24.08
2.	2.	100.	60′	100°c.d.	..	..	..	..	..	8.65	..	..	..	6.06	..	..	24.70
2.	2.	100.	60′	40°	..	..	..	9.46	..	10.56	..	28.67	..	6.81	..	..	24.98

In explanation of the table it must be said that the Navassa and South Carolina phosphates, with the exception of Navassa

No. 12, were supplied by the committee of the convention. The Navassa No. 12 was a specimen on hand for about six months in the laboratory of the Department of Agriculture, but from a like source as the others. The precipitated phosphate, which is introduced for comparison, was a commercial article, consisting of a mixture of di- and tricalcic phosphates. In the series for temperature, that marked 100° c.d. means that the flask was introduced into a copper water-bath containing three hundred cubic centimetres of boiling water and allowed to cool down for the time given.

There is also given a determination of the amount of phosphoric acid in the acid phosphates left undissolved on treatment with citrate in the usual way.

The obvious conclusions from these results are that the amount of phosphoric acid dissolved is entirely dependent on the time and temperature of digestion and concentration of solution; that while for any one fertilizer the citrate and oxalate methods may be made to agree by a suitable arrangement of conditions, no such arrangement will be suitable to even two fertilizers of one class, as is shown by the two samples of Navassa acid phosphates. The advantage, then, of oxalate over citrate does not appear except in its more energetic action, which could be also brought about in the use of citrate by an increase in the concentration of solution or of the time and temperature of digestion.

In bone superphosphates, owing to their simple composition, it is possible to arrange the conditions for the use of either citrate or oxalate to produce an accurate separation; but with the more complicated mineral superphosphates, in every sample of which the relative amount of iron changes, any such selection of proper conditions is impossible, and the only thing, until some better method can be discovered, will be to agree upon some mode of treatment of ferruginous phosphates which will, for the average, approach most nearly to the truth.

I am indebted to Mr. A. E. Knorr for a large number of the determinations in this paper.

WASHINGTON, *Jan.* 1882.

ON SOME DERIVATIVES OF p-OXY-m-TOLUIC ACID.

By R. W. Mahon.

This acid has been obtained by Tiemann and Schotten[1] and by Remsen and Iles,[2] and is known to have the structure represented by the formula $C_6H_3\begin{cases}OH & (1)\\ CH_3 & (2)\\ COOH & (4)\end{cases}$. It is most easily prepared according to the directions given by Remsen and Iles, viz. by oxidizing α-xylenesulphamide and fusing the resulting sulphaminetoluic acid with potassium hydroxide. I have prepared a considerable quantity of the acid, and studied a few of its derivatives which are described in this paper. The acid itself crystallizes in beautiful, long, colorless needles resembling salicylic acid. It contains half a molecule of water of crystallization. After drying at 120°, it fuses at 174.5° (corrected).

It was heated with ordinary concentrated nitric acid, for the purpose of converting it into a nitro-derivative. This operation, to be successful, must be conducted as follows: Quantities not exceeding a gram must be used, and boiled in the acid until perfectly dissolved. The action must then be instantly checked by plentiful dilution with water and rapid cooling. By working in this manner a series of yields were obtained, which consisted of fine glistening yellow needles. This material is extremely soluble in alcohol, especially when hot, yielding an intensely yellow solution, and from this solution it can be obtained in fine needles. Determination of the fusing point of this recrystallized product gave 86°–87° (corrected). This material is not very soluble in water, and is volatile with water vapor. In ether it is very soluble.

Calcium Nitro-oxytoluate, $(C_6H_2.OH.CH_3.NO_2.CO_2)_2Ca+4H_2O$. This was prepared by boiling the nitro-acid with finely pulverized calc spar. It is quite soluble in water, yielding an intensely red solution, and crystallizes in aggregations of fine gold yellow needles. These, when rendered anhydrous by heating, turn to an orange

[1] Berichte der deutschen chemischen Gesellschaft, **11**, 767. [2] This Journal, **1**, 32.

color, and the anhydrous salt is slightly hygroscopic. The salt explodes when heated.

I. 0.2999 gram salt lost 0.0429 gram water of crystallization.

II. 0.1753 gram salt gave 0.0453 gram $CaSO_4$.

	Calculated.		Found.	
			II.	II.
$C_{16}H_{12}N_2O_{10}$	392	77.77	...	...
Ca	40	7.94	...	7.60
$4H_2O$	72	14.29	14.31	...
		100.00		

Barium Nitro-oxytoluate, $(C_6H_2.OH.CH_3.NO_2.CO_2)_2Ba+4H_2O$. This was prepared by boiling the acid with pure barium carbonate. It is quite soluble in water, yielding a red solution. From the solution it crystallizes in star-like aggregations of fine orange yellow needles. The anhydrous salt is of an intense crimson color, and somewhat hygroscopic. The salt explodes when heated.

I. 0.4031 gram salt gave up 0.0165 gram water of crystallization.

II. 0.2701 gram salt gave 0.1049 gram $BaSO_4$.

	Calculated.		Found.	
			II.	II.
$C_{16}H_{12}N_2O_{10}$	392	65.24	...	...
Ba	137	22.78		22.83
$4H_2O$	72	11.98	11.54	...
		100.00		

When the crystals of the nitro-acid are heated in water, part dissolves, and an oil is formed of a brownish yellow color. This oil is difficult to get into solution, and it was at first thought that there were two products formed when nitric acid acts on oxytoluic acid. That the crystals, and the oil, which is a solid yellow mass when cooled, are the same substance, was proved by the identity of their fusing points. Both the oil and the crystals dissolve in ammonia, yielding a red solution, which contains the ammonium salt of the nitro-derivative. Caustic soda added to this solution causes the evolution of ammonia. Hydrochloric acid re-precipitates the nitro-acid. This ammonium salt crystallizes out of solution in fine yellow needles, which cover the vessel in arborescent shapes. It turns to an orange color when rendered hygroscopic,

and explodes when more strongly heated. The sodium salt also crystallizes in fine needles. These are of an orange color, and turn to a redder tint when heated. This salt also is explosive. Both the sodium and the ammonium salt are quite soluble in water. When the nitro-acid is thrown down by the addition of a stronger acid to a solution of one of its salts it is pure white, but it rapidly turns yellow. All the salts, as well as the acid itself, have marked tinctorial power.

JOHNS HOPKINS UNIVERSITY, *May*, 1882.

NOTE ON THE AMMONIA-PROCESS FOR WATER ANALYSIS.

BY CHARLES W. MARSH.

The present article contains the results of some investigations in connection with a systematic examination and comparison of various methods of water analysis. Among other questions presented for examination was that of the possible loss of volatile organic matter during the evaporation and boiling of water, necessitated by the ammonia and other processes. At the suggestion of Prof. Cornwall the series of experiments in Table I was begun last fall. After the experiments had been nearly completed, a copy of a "Report on a Peculiar Condition of the Water of Boston in November, 1881," by Prof. Ira Remsen, was received, in which it was found that Prof. Remsen had already anticipated the results here given in his report, in which he says: "Another fact which came out in the examination of the Baltimore water was this: When free and 'albuminoid ammonia' were determined by the method already described, the amounts of the two added together were found to be considerably smaller than the total ammonia found when the oxidizing mixture was added at the beginning of the operation, before the water was boiled. This

clearly indicated that in the first stage of the process, as usually conducted, there passed over with the free ammonia some nitrogenous substance capable of yielding ammonia with permanganate of potash. As this distillate had a strong odor, something like the 'cucumber odor,' the suggestion was made that the odor of the water was due to the presence of some volatile nitrogenous substance, the special nature of which could not be determined. The examination of the Farm-pond water confirms this idea. One example will make this clear, and will suffice: a specimen of Farm-pond water gave, when examined in the usual way, 0.034 free and 0.274 albuminoid ammonia, making a total of 0.308 parts of ammonia in 1,000,000 parts of water. When the same water was treated at the outset with the oxidizing mixture, it gave a total of 0.506 parts of ammonia. There remains here the difference between 0.308 and 0.506 to be accounted for, or two-fifths of the total. The material capable of yielding this lost ammonia was undoubtedly lost in the distillations of the water for free ammonia, and it must hence be a volatile nitrogenous substance."

The analyses in Table I may still prove of interest, both as verifying his statement and illustrating the great variability in the proportion of organic matter which may thus be lost. Twenty-six analyses were made on different waters, proceeding in the following manner: The analysis for free and albuminoid ammonia was made as Wanklyn directs. Then 300 cc. were taken (the same quantity remaining in the retort when the permanganate of potash is added in the regular analysis), and 50 cc. of permanganate were added, and three distillates of 50 cc. each were taken off and nesslerized, and the whole calculated to one litre. This gave the total ammonia. In only one case did the sum of the free and albuminoid ammonia exceed the total ammonia. In three cases the results were identical, and in the other twenty-two the total ammonia was more than the sum of the free and albuminoid ammonia. In Table I in the first column is the free ammonia; in the second the albuminoid ammonia; in the third the sum of the two; in the fourth the total ammonia; and in the fifth the difference between the total ammonia and the sum of the free and albuminoid ammonia.

TABLE I.

No.	Specimen.	Free Ammonia.	Albuminoid Ammonia.	Sum of Free Ammonia and Albuminoid Ammonia.	Total Ammonia.	Difference bet. Sum of Free Ammonia and Alum'oid Am. and Total Am.
1	Well Water	.04	.15	.19	.29	.10
2	" "	.05	.20	.25	.35	.10
3	" "	.05	.10	.15	.18	.03
4	Cistern "	.01	.07	.08	.10	.02
5	" "	.01	.06	.07	.07	.00
6	" "	.09	.07	.16	.18	.02
7	Well "	.46	.07	.53	.56	.03
8	Canal "	.01	.20	.21	.21	.00
9	Distilled Water.....	.36	.03	.39	.49	.10
10	Well Water	.01	.04	.05	.07	.02
11	" "	.06	.08	.14	.16	.02
12	Spring "	.06	.08	.14	.15	.01
13	Surface "	8.10	1.75	9.85	10.12	.27
14	" "	2.84	1.46	4.30	4.10	*.20
15	" "	8.48	2.12	10.60	11.11	.51
16	Cistern "	.07	.08	.15	.18	.03
17	Well "	.02	.16	.18	.20	.02
18	" "	.02	.07	.09	.10	.01
19	" "	.01	.02	.03	.07	.04
20	Spring "	.01	.02	.03	.06	.03
21	Well "	.02	.03	.05	.06	.01
22	" "	.11	.11	.22	.24	.02
23	" "	.01	.04	.05	.10	.05
24	" "	.16	.11	.27	.34	.07
25	" "	.07	.08	.15	.20	.05
26	" "	.04	.08	.12	.12	.00

The ammonia is expressed in parts per million.

It will be seen from the table that No. 14 was the only water where the sum of the free and albuminoid ammonia was greater than the total ammonia. This exceptional result may well be ascribed to the greater difficulty of accurately estimating the ammonia in highly colored nesslerized solutions, and to the fact that any actual errors of this kind were increased in calculating the results, since it was necessary to dilute the specimen very largely with water free from ammonia. In Nos. 5, 8 and 26 it appears that no volatile nitrogenous substance escaped, as will be seen from the last column. All the other waters show different amounts of gain of the total ammonia over the sum of the free and albuminoid ammonia, some slight and some comparatively very large. The results in the table conclusively prove that something escapes con-

version into ammonia. Is this something which escapes condensation, or will it be found in the distillate? To decide this question 500 cc. of the water were boiled as usual to obtain a distillate of 200 cc., containing, according to Wanklyn, all the free ammonia. This distillate was redistilled with a proportionate amount of permanganate (33 cc.), and two distillates of 50 cc. each were obtained and nesslerized, the result being doubled to bring it up to one litre. This gave all the free ammonia and any ammonia which may come from the action of the permanganate on any condensible, nitrogenous, organic compound which had come over with the free ammonia. The ammonia from these two sources is given in the next to the last column Table II. In this table are the results of analysis on ten samples of water. In the first four columns the data are the same as in Table I. In the fifth column is the free ammonia and the ammonia which we have regained. In the sixth column is the sum of the albuminoid ammonia and the ammonia in the fifth column.

TABLE II.

No.	Specimen.	1 Free Ammonia.	2 Albuminoid Ammonia.	3 Sum of Free Am. and Alb. Am.	4 Total Ammonia.	5 Sum of Free Am. and Regained Am.	Sum of 2 and 5.
1	Well Water...	.04	.10	.14	.19	.06	.16
2	" " ...	.05	.10	.15	.16	.06	.16
3	" " .	.05	.08	.13	.17	.09	.17
4	" " ...	.04	.07	.11	.12	.06	.13
5	" " ...	.04	.07	.11	.12	.05	.12
6	" " ...	.05	.22	.27	.27	.05	.27
7	" " ...	.03	.12	.15	.17	.06	.18
8	" " ...	.04	.03	.07	.08	.05	.08
9	Cistern " ...	.05	.11	.16	.22	.08	.19
10	Well " ..	.02	.08	.10	.15	.07	.15

The ammonia is expressed in parts per million.

It would appear that in the case, at least, of specimens Nos. 2, 3, 5, 6, 8 and 10, the excess of ammonia obtained where the whole of the water was distilled with the permanganate directly, over the sum of the free and albuminoid ammonia as usually obtained, was due to some volatile, condensible, nitrogenous compound, from

which as much ammonia could be obtained by the action of boiling permanganate after its distillation from the original water, as before. In Nos. 1 and 9 the sum of the albuminoid ammonia and the ammonia from the redistillation is less than the total ammonia, hence some of the constituents escaped in the first distillation. In Nos. 4 and 7 the sum of the two ammonias in the sixth column is slightly greater than the total ammonia, which may be due to error of reading; at all events these two waters would show that all the ammonia was regained.

It is possible that the modification of the usual ammonia-process which is obviously suggested by the foregoing experiments may reconcile the differences now existing between the organic purity of water as determined by the ammonia-process, and the oxidation process with permanganate (Forchammer's and its modifications). Work in this direction is now going on.

John C. Green School of Science, Princeton, N. J., *March* 16, 1882.

ON THE BENZOYL DERIVATIVES OF THE XYLENE-SULPHAMIDES.

By R. W. Mahon.

It has been shown by the investigations of Remsen and Iles[1] and of Jacobsen[2] that the α- and β-sulphamides obtained from meta-xylene have respectively the formulas

$$C_6H_3\begin{cases}SO_2NH_2 & (1)\\ CH_3 & (2)\\ CH_3 & (4)\end{cases} \quad \text{and} \quad C_6H_3\begin{cases}SO_2NH_2 & (1)\\ CH_3 & (2)\\ CH_3 & (6)\end{cases}$$

As in the β-amide both methyl groups are in the ortho-position relatively to the sulphamide group, its conduct toward oxidizing agents is a matter of considerable interest. According to the law discovered by Professor Remsen, the validity of which has been established by a large number of investigations which have been carried on in this laboratory, it would appear that both the methyl

[1] This Journal, **1**, 32. [2] Berichte der deutschen chemischen Gesellschaft, **10**, 1009.

groups ought to be protected when the amide is subjected to the influence of acid oxidizing agents. But it is stated by Jacobsen[1] that this amide conducts itself in the same way as the α-amide, yielding by oxidation with chromic acid a monobasic acid. His proofs are, however, wholly unsatisfactory, and Professor Remsen has shown[2] that the statement cannot be strictly correct. In view of the importance of the subject it seemed desirable to obtain a considerable quantity of the β-amide in pure condition and study its conduct carefully. Its separation from the α-amide by crystallization is extremely difficult, and but very small quantities can be obtained in this way. I have hence tried to effect the separation by the aid of the benzoyl derivatives. As Wolkow[3] has shown that the benzoyl derivatives of the sulphamides of toluene have markedly acid properties, it was hoped that the corresponding derivatives of xylene might yield salts which could be separated by crystallization.

Quantities of the mixed amides were heated with benzoyl chloride, in the proportion of their molecular weights, at a temperature of 150°–160°, in an oil-bath, until gas ceased to be given off. The black cakes left in the flasks were found to be insoluble in water and in ether; they dissolved easily in hot alcohol. The product was recrystallized from water and alcohol, and thus obtained in short colorless needles. Its fusing point was determined to be 149°–151° (uncorrected). This recrystallized product, when heated with alcoholic potash, yielded the simple α-xylenesulphamide. It also dissolved easily in ammonia, and from the ammoniacal solution, the addition of an excess of hydrochloric acid threw down a precipitate. To another portion of the ammoniacal solution, after the excess of ammonia had been driven off, barium chloride was added, causing the precipitation of a white crystalline material. This material proved to be a barium salt. Some of the acid precipitated from the solution of the ammonium salt was boiled with barium carbonate, and a barium salt was obtained in this way.

Estimations of barium and of water of crystallization were made in these materials, viz. that obtained by boiling with barium carbonate, and that precipitated by barium chloride from an ammoniacal solution of the material of fusing-point 149°–151°.

[1] Berichte der deutsch. chem. Gesellschaft, **11**, 893.
[2] This Journal, **1**, 32.
[3] Zeitschrift für Chemie, N. F. **6**, 577.

Barium α-xylenesulph-benzoyl-amide, $\left(C_6H_3\begin{vmatrix}CH_3\\CH_3\\SO_2N.C_7H_5O\end{vmatrix}\right)_2Ba.$

Crystallizes out of solution in fine colorless needles and is difficultly soluble in water.

1. 0.1207 gram salt lost no water at 155°, and gave 0.0391 gram $BaSO_4$.

2. 0.2734 gram salt lost no water at 125°, and gave 0.0886 gram $BaSO_4$.

3. 0.1349 gram salt lost no water, and gave 0.0438 gram $BaSO_4$.

		Calculated.	Found.		
			I.	II.	III.
$C_{30}H_{28}S_2N_2O_6$	576	80.79	...	...	...
Ba	137	19.21	19.66	19.05	19.09
		100.00			

Calcium α-xylenesulph-benzoyl-amide, $\left(C_6H_3\begin{vmatrix}CH_3\\CH_3\\SO_2N.C_7H_5O\end{vmatrix}\right)_2Ca + H_2O.$ Crystallizes out of solution in fine colorless needles. It was prepared by boiling the acid with finely pulverized calc spar. This salt is difficultly soluble in water. The barium and calcium salts are about equally soluble. The calcium salt is soluble in alcohol and in ether. When recrystallized from alcohol it has the molecule of water of crystallization; this is true of the salt recrystallized from water also.

1. 0.31745 gram salt lost 0.009 gram water at 147°, and gave 0.06785 gram $CaSO_4$.

2. 1.0161 gram salt lost 0.0285 gram water at 150°, and gave 0.2129 gram $CaSO_4$.

		Calculated.	Found.	
			I.	II.
$C_{30}H_{28}N_2S_2O_6$	576	90.85	...	...
H_2O	18	2.84	2.84	2.80
Ca	40	6.31	6.29	6.16
		100.00		

Thus it will be seen that when the α-amide is heated with benzoyl chloride, a compound amide is formed, in which one atom of hydrogen in the amido group has been replaced by benzoyl, and

in which the remaining hydrogen atom possesses acid properties. The reaction is represented by the equation—

$$C_6H_3\begin{cases}CH_3\\CH_3\\SO_2NH_2\end{cases}+C_6H_5CO.Cl=C_6H_3\begin{cases}CH_3\\CH_3\\SO_2NH.C_7H_5O\end{cases}+HCl.$$

When mixtures of the *α*- and *β*-amides (containing a large proportion of the latter) were heated with benzoyl chloride and the product dissolved in ammonia, the subsequent addition of an excess of hydrochloric acid caused the separation of a gummy mass, the gummy character of which was the more marked the more of the *β*-amide was present in the mixture acted on by the acid chloride. It was from such a gummy mass that by recrystallization from alcohol, the *α*-benzoylamide, a well characterized crystalline substance of fusing point 149°–151°, was obtained. After the removal of several crops of crystals of the *α*-benzoylamide from the alcoholic solution had been effected by stopping the evaporation of the solution at intervals, the subsequent evaporation to near dryness caused the deposition of a material of an oily nature, which solidified to a clear brownish yellow gum, holding crystals of the *α*-benzoylamide enclosed in it. From these experiments it is seen that when benzoyl chloride acts on a mixture of the *α*- and *β*-sulphamides of xylene, there are formed two products: *α*-benzoylamide, and an oil which is more soluble in alcohol than *α*-benzoylamide.

The following facts seem to indicate that the oily substance is the *β*-benzoylamide. It is easily soluble in ammonia or an alkaline carbonate, and from such solution an excess of hydrochloric acid precipitates the original oil; when boiled in water with pulverized calc spar and filtered, the addition of hydrochloric acid to a portion of the filtrate precipitates the original oil, and calcium is easily shown to be present; a solution which was shown to contain a barium salt is also similarly prepared with barium carbonate. If these various solutions be evaporated, an oil is in each case deposited, which is found to be insoluble in ammonia or alkaline carbonates; these being, as already suggested, probably salts of the compound amide. The oils, or gums, examined, especially the original gum, and the result of boiling that with calc spar, were found to themselves possess the property of dissolving the crystals

of the α-amide, and a part of these crystals separated out on cooling. Quantities of oil holding apparently no crystalline material were allowed to stand for days over concentrated sulphuric acid, when a considerable crop of crystals made their appearance. All of the simple α- and β-amides at hand were now heated with benzoyl chloride in the proportion of their molecular weights, and at the temperature mentioned above (150°–160°). The material was divided into two parts, that consisting mostly of α-amide and that consisting mostly of β-amide; and these were worked up separately. By repeated crystallizations of the product from alcohol, the supposed β-benzoylamide was obtained in a condition of considerable purity. This purified product was boiled with finely pulverized calc spar. After filtering, the gummy calcium salt above mentioned was obtained from the filtrate, with some crystalline material, the calcium salt of the α-benzoylamide. This oily material was dissolved in water, in which it is difficultly soluble, and the addition of hydrochloric acid to its solution caused the separation of the β-benzoylamide. By further heating in water more crystals were mechanically separated. This process of mechanical separation having been several times repeated, the β-benzoylamide was obtained in a comparatively pure condition, although, owing to the solubility of the α in the β compound, not entirely so. Hence no attempt was made to analyze the salts. It was thought that nearly pure β-amide could probably be obtained from the purified oil. As the α-benzoylamide is decomposed readily by boiling with alcoholic potash yielding the simple amide quantitatively, the effect of this reagent was first tried on the β compound. As far as could be judged no effect was produced, certainly no β-sulphamide was obtained. It was then boiled with concentrated hydrochloric acid, without effecting its decomposition. The α-benzoylamide is also undecomposed by boiling with concentrated hydrochloric acid. Quantities of the β-benzoylamide were heated with concentrated hydrochloric acid in sealed tubes, without yielding the simple amide. When heated at 169° for several hours, with a large excess of concentrated hydrochloric acid, the gum entirely disappeared; but careful examination failed to detect any simple β-amide in the product. The action of concentrated sulphuric acid on the β-benzoylamide was also studied, but no decomposition into simple amide noticed. Owing to this extreme and unexpected stability of the β compound, the attempt

to prepare the simple amide from the material employed in this investigation was unsuccessful. It must be said that notwithstanding the general properties of the oily product above described, its stability makes it appear doubtful whether it really was the β-benzoylamide. It may have been some other product of the action of benzoyl chloride on the β-sulphamide.

JOHNS HOPKINS UNIVERSITY, *May*, 1882.

ON THE OXIDATION OF SUBSTITUTION PRODUCTS OF AROMATIC HYDROCARBONS.

XII.—PROTECTION OF A GROUP CONTAINING TWO CARBON ATOMS.

BY IRA REMSEN AND W. A. NOYES.

That negative atoms or groups in the ortho-position relatively to methyl protect the latter from the influence of the oxidizing action of chromic acid may now be regarded as established. The questions naturally suggest themselves: (1) Can these same groups protect ethyl, propyl, and more complex residues? (2) How far does this protective influence extend? or, in other words, if larger residues than methyl are protected, what is the largest which can thus be protected? There are very few, if any, facts recorded which can aid us in forming a conclusion. The case described by von Gerichten[1] some time since, to which attention was called in an earlier paper of this series, has perhaps some bearing on the questions. This author obtained a chlorcymene by treating thymol with phosphorus pentachloride. In the product the chlorine atom should be in the ortho-position relatively to the propyl group. By oxidation with nitric acid this chlorcymene yields an acid having the empirical formula of a chlor-propyl-benzoic acid. It appeared probable that the formation of this acid might be explained by supposing that the chlorine protects the entire propyl group and that the para-methyl is transformed into carboxyl. Later, von Gerichten states that his acid is not

[1] Berichte der deutschen chemischen Gesellschaft, **11**, 365. 1719.

chlor-propyl-benzoic acid, but that the carboxyl is in the propyl. The acid is, according to him,

$$C_6H_3\begin{cases}CH_3 & (1)\\ Cl & (3)\\ C_3H_4CO_2H & (4)\end{cases}, \text{ and not } C_6H_3\begin{cases}CO_2H & (1)\\ Cl & (2)\\ C_3H_7 & (4)\end{cases}$$

One of us has already criticized the paper of von Gerichten and shown that his view is very improbable. At the same time his statements have not been disproved, nor has he in any way modified them since. There is one other case of a somewhat similar character which should be referred to. Aschenbrandt[1] has shown that when para-diethyl-benzene is treated with nitric acid, two effects are produced—a nitro group is introduced into the compound and one ethyl group is changed to carboxyl. It is impossible, however, from the experiments described to determine (1) whether the nitro group enters the hydrocarbon first, and the nitro product is then oxidized; (2) whether the oxidation first takes place, and the nitro group then enters the acid; and (3) what the structure of the nitro-ethyl-benzoic acid is. It appears probable that the nitro group first enters the hydrocarbon, and that then oxidation takes place. But the formation of nitro-ethyl-benzoic acid under the circumstances described would not prove that the nitro-group protects the ethyl, for the reason that, as a rule, nitric acid has the power to oxidize only one of two paraffin residues contained in an aromatic hydrocarbon, whether a negative group is present or not. So, also, whatever may be the nature of von Gerichten's acid, it must be borne in mind that it is formed by oxidizing with nitric acid, and, as yet, very little is known in regard to the action of this agent. The main question at present is simply: How does *chromic acid* act on compounds in which there are negative groups in the ortho-position relatively to paraffin residues of greater complexity than methyl?

It is not an easy matter to get substitution-products which furnish the necessary conditions for an investigation of the kind proposed. It appears to be highly probable that, when negative groups enter aromatic hydrocarbons in which there are two paraffin residues of different composition, the substitution takes place in the ortho-position relatively to the residue containing the smaller number of carbon atoms. Thus, when cymene, $C_6H_4\begin{cases}CH_3,\\ C_3H_7\end{cases}$ is

[1] Berichte der deutschen chemischen Gesellschaft, **12**, 1304.

treated with bromine, chlorine, nitric acid, or sulphuric acid, the product in each case contains the substituting atom or group in the ortho-position relatively to methyl. Paterno,[1] Spica[2] and Claus[3] have indeed shown that when sulphuric acid acts on cymene, the second possible sulphonic acid, viz. $C_6H_3\begin{cases}CH_3 & (1)\\ SO_3OH & (3),\\ C_3H_7 & (4)\end{cases}$ in which the sulpho-group is ortho relatively to propyl, is formed, but, under ordinary circumstances, in very small quantity. The experiments of Morse and Remsen[4] also seem to indicate that, when para-ethyl-toluene is treated with bromine, that product is formed in which the bromine is ortho relatively to methyl. In order, therefore, to secure a substance containing a substituting group in the ortho-position relatively to a residue more complex than methyl, we started from para-diethyl-benzene. This was converted into the sulphonic acid. From the acid the corresponding amide was prepared, and this was subjected to oxidation.

In the preparation of diethyl-benzene the directions of Aschenbrandt[5] were followed. The greatest precautions were taken, but still the yield was small. The reaction is by no means as clean as that which takes place between dibrom-benzene and methyl iodide. We used in some experiments ethyl bromide, in others ethyl iodide. The yield was somewhat better when the former was used. Most of the ether used had been standing in contact with metallic sodium for nearly a year, and had previously served in the synthetical preparation of para-xylene. The largest amount of bibrom-benzene used in any one experiment was 50 grams. This was mixed with about one-fourth more than the theoretical quantity of ethyl bromide or iodide. The mixture was kept cool by ice. The reaction took place slowly and required about twenty-four hours for its completion. We obtained only about thirty grams of the desired product instead of one hundred and seventy grams required by theory. The hydrocarbon boiled at 183° (uncorrected). Aschenbrandt[6] gives 181°–182°, and Fittig[7] 178°–179° as the boiling point.

[1] Gazetta chimica italiana, **4**, 115.
[2] Berichte der deutschen chemischen Gesellschaft, **14**, 652.
[3] *Ibid.* **13**, 901, 2044; and **14**, 2139.
[4] This Journal, **1**, 138.
[5] Berichte der deutschen chemischen Gesellschaft, **12**, 1303.
[6] *Loc. cit.*
[7] Annalen der Chemie, **144**, 285.

Sulphamide of Diethyl-benzene.

About twenty grams of the hydrocarbon were treated with 75 to 100 grams of fuming sulphuric acid. Solution took place readily with considerable evolution of heat. To complete the action the whole was finally heated for a short time on a water-bath. On diluting with water, neutralizing with pure barium carbonate, filtering and concentrating to about 500 cc., a quantity of the barium salt crystallized out. This was recrystallized and analyzed.

0.3600 gram of the air-dried salt lost 0.401 gram H_2O at 150° and gave 0.1316 gram $BaSO_4$.

		Calculated.	Found.
$(C_{10}H_{13}SO_2)_2$	426	67.09	...
Ba	137	21.57	21.49
$4\,H_2O$	72	11.34	11.14

The solubility of the salt was determined by Victor Meyer's method.

1.1887 gram of a solution saturated at 23° gave 0.0577 gram of the anhydrous salt dried at 140°.

100 parts of water at 23° dissolve 5.1 parts of the anhydrous salt.

The formula of the salt is seen to be $\left\{ C_6H_3 \left\{ \begin{matrix} (C_2H_5)_2 \\ SO_2O \end{matrix} \right\} \right\}_2 Ba + 4H_2O$. It crystallizes well in small leaflets with a beautiful pearly lustre. The water of crystallization is given off almost entirely at 102°. Fittig, who has prepared the salt, does not mention the water of crystallization nor the fact that the salt crystallizes. Probably he had but a very small quantity of it in impure condition, as it crystallizes very readily when pure.

The barium salt was converted into the potassium salt, and the latter evaporated to dryness and converted into the amide by the usual reactions. The conversion of the chloride into the amide took place with difficulty. Prolonged heating with concentrated aqueous ammonia was necessary, while ammonia gas was passed through the liquid. The amide was easily purified by recrystallization from water, in which it is difficultly soluble. It fuses under water below the boiling point. It crystallizes in small leaflets and is colorless. It fuses at 97.5° (corrected). The analyses gave results as follows:

I. 0.01565 gram of the amide gave 0.001045 gram N. (Frankland's method.)

II. 0.2167 gram gave 0.01469 gram N.
III. 0.1011 gram gave 0.1131 gram $BaSO_4$. (Liebig's method.)

	Calculated.		Found.		
			I.	II.	III.
C_{10}	120	56.34	...	...	...
H_{15}	15	7.04	...	...	...
N	14	6.58	6.68	6.78	...
S	32	15.02	...	...	15.36
O_2	32	15.02	...	...	...

The method of preparation and the results of the analyses show that the substance is $C_6H_3\begin{cases}C_2H_5 & (1)\\ SO_2NH_2 & (2)\\ C_2H_5 & (4)\end{cases}$

Oxidation of Para-diethyl-benzene-sulphamide.
Sulphamine-ethyl-benzoic acid.

The amide was treated with chromic acid in these proportions: 24 grams of potassium pyrochromate, 36 grams of concentrated sulphuric acid, diluted with three volumes of water, and 5 grams of the amide. The whole was heated over a small free flame for about an hour. On cooling, a well crystallized substance was deposited. The whole was diluted with water and filtered. The acid remaining in the filter was well washed out, and then treated with dilute sodium carbonate, in order to separate the acid from some unchanged amide. The solution was boiled and evaporated down to a small volume, when the amide crystallized out. This was filtered off, and the acid precipitated from the filtrate by the addition of hydrochloric acid. By dissolving in water, boiling with animal charcoal, filtering, and allowing to cool, the acid was obtained in beautiful, long, colorless needles. This is, however, not perfectly pure, as the amide is much more soluble in an alkaline than in an acid solution. The acid was finally obtained in perfectly pure condition by preparing the barium salt and recrystallizing this. It fuses at 261°–262° (corrected), at the same time undergoing slight decomposition.

The analyses gave the following results:

I. 0.0141 gram gave 0.000906 gram N (Frankland's method).
II. 0.1069 gram gave 0.1101 gram $BaSO_4$ (Liebig's method).

	Calculated.		Found. I.	II.
$C_9H_{11}O_4$	183	79.91	...	...
S	32	13.98	...	14.14
N	14	6.11	6.48	...
	229	100.00		

It is at least evident from these results that both the ethyl groups have not been oxidized to carboxyl. Disregarding any preconceived notions concerning protection, there are four possible products to be decided between. These are:

(1) $C_6H_3\begin{cases}COOH\\SO_2NH_2\\COOH\end{cases}$; (2) $C_6H_3\begin{cases}CH_2COOH\\SO_2NH_2\\COOH\end{cases}$; (3) $C_6H_3\begin{cases}CH_3\\SO_2NH_2\\COOH\end{cases}$;

and (4) $C_6H_3\begin{cases}C_2H_5\\SO_2NH_2\\COOH\end{cases}$. Formula (1) requires 5.71 per cent. N and 13.06 per cent. S; and formula (2) still less, so that these are excluded at once. Of the two others (3) requires 6.51 per cent. N and 14.88 per cent. S. When we consider the difficulties involved in making accurate estimations of nitrogen and sulphur in substances of the kind with which we are dealing, the results obtained by us can hardly be considered as positive evidence against formula (3), though they agree much better with those required by formula (4). Finally, the barium salt was prepared, and every precaution taken to secure it in a state of perfect purity. It is easily soluble in water, and crystallizes in needles, which we were not able to free from a slight yellow color. The dried salt was finely pulverized, and treated with a little strong alcohol for the purpose of dissolving any traces of the original amide. It was then washed on the filter with alcohol, dried, and recrystallized from water. It crystallized as before in fine concentrically grouped needles, with a slight yellow color. Two analyses were made with the following results:

I. 0.1984 gram of the air-dried salt lost 0.0388 gram H_2O at 150°, and gave 0.0624 gram $BaSO_4$.

II. 0.2748 gram air-dried salt lost 0.0512 gram H_2O at 150°, and gave 0.0876 gram $BaSO_4$.

The results with the water of crystallization do not agree, as will be seen:

		Found. I.	II.
Calculated for $\left(C_6H_3\begin{cases}C_2H_5\\SO_2NH_2\\CO_2\end{cases}\right)_2Ba+3H_2O$.			
H_2O	19.54	19.56	18.63

The salt used for the second analysis had stood for twenty-four hours in a very dry and warm room, and had evidently lost some of its water, as its appearance indicated slight efflorescence. The barium estimations, however, calculated on the basis of the anhydrous salt, agree excellently, and leave no room for doubt regarding the composition of the salt.

Calculated for $\left(C_6H_3\begin{cases}C_2H_5\\SO_2NH_2\\CO_2\end{cases}\right)_2Ba$.		Found. I.	II.
Ba	23.10	23.00	23.03

It is clear then that the salt is derived from sulphamine-ethyl-benzoic acid, $C_6H_3\begin{cases}C_2H_5\\SO_2NH_2\\COOH\end{cases}$, and not from sulphamine-toluic acid $C_6H_3\begin{cases}CH_3\\SO_2NH_2\\COOH\end{cases}$. The anhydrous barium salt of the latter acid requires 24.25 per cent. barium.

The presence of the sulphamine group prevents the oxidation of the ethyl group by chromic acid, just as it has been found to prevent the oxidation of the methyl group in the many cases studied.

While from the experiments described the fact is established that the sulphamine group exerts a protective influence on the ethyl group, they do not show whether these two groups are in the ortho-position relatively to each other or not. Analogy indicates that they do stand in this relation, but it is desirable to furnish independent proof of the fact.

The sulphamine group must be either in the ortho- or the meta-position relatively to the carboxyl. If it were in the ortho-position, the substance obtained by oxidation should belong to the class called sulphinides, and have the formula $C_6H_3\left\{\begin{matrix}C_2H_5\\SO_2\\CO\end{matrix}\right\}NH$. This statement is based on the fact that in every case known in which the sulphamine and carboxyl groups are in the ortho-position relatively to each other, the corresponding sulphinide is formed. The analyses of the free acid given above, though they are perhaps not conclusive, indicate that it is the acid and not the sulphinide. The latter requires 6.64 per cent. N and 15.17 per cent. S; while the results found are 6.48 per cent. N and 14.14 per cent. S. As far as our experiments are concerned the question as to the

relative position of the sulphamine and carboxyl groups must be regarded as to some extent an open one, though, as will be clear, there is a strong probability in favor of the view that the relation is that which is commonly called ortho.

Oxidation of Sulphamine-ethyl-benzoic Acid with Potassium Permanganate.

It has been shown by previous experiments[1] that when sulphamine-para-toluic acid is oxidized with potassium permanganate in slightly alkaline solution, terephthalic sulphinide, or rather its potassium salt, $C_6H_3\begin{cases}CO_2K\\CO\\SO_2NH\end{cases}$ $+H_2O$, is formed. The same product should be formed from the sulphamine acid above described.

One gram of the acid was dissolved in a slight excess of potassium hydroxide and added to a solution of six grams of potassium permanganate in 100 cc. of water. The mixture was heated for twelve hours on the water-bath. The permanganate was completely decolorized. The oxides of manganese were filtered off, the filtrate evaporated to about 75 cc., and acidified with hydrochloric acid. After standing for some time, a white substance crystallized out in fine needles. Analysis I, given below, was made with this portion. On evaporating the mother-liquor and allowing it to cool, a second portion crystallized out. This was filtered off and well washed with water. This was used for analysis II.

I. 0.2795 gram of portion I lost 0.0164 gram H_2O at 150°, and gave 0.0821 gram K_2SO_4. This salt gave a marked reaction for nitrogen with soda-lime.

II. 0.1269 gram of portion II lost 0.0075 gram H_2O at 150°, and gave 0.0365 gram K_2SO_4. This salt gave only a slight reaction for nitrogen with soda-lime.

	Calculated for $C_6H_3\begin{cases}CO\\SO_2NH\\CO_2K\end{cases}+H_2O$.	Found. I.	Found. II.	Calculated for $C_6H_3\begin{cases}CO_2H\\SO_2K\\CO_2H\end{cases}+H_2O$.
K	13.81	13.17	12.92	12.94
H_2O	6.36	5.87	5.91	5.96

The results of the analyses together with the nitrogen tests show that the first specimen contained some of the nitrogenous substance,

[1] See Remsen and Hall, this Journal, **2**, 58.

but that the second specimen was nearly pure mono-potassium sulpho-terephthalate. Its properties were the same as those of this salt as given by Remsen and Hall.[1] Although we worked under the same conditions as they did, we plainly obtained a mixture of the two products. This may possibly be explained by the fact that in the case of the ethyl compound a quantity of carbonic acid is formed by the oxidation of a part of the ethyl group, and Fahlberg[2] has shown that in a similar case the presence of carbonic acid was sufficient to prevent the formation of the sulphinide and cause the formation of the corresponding sulphonic acid. The small quantity of material at our disposal prevented us from following this inquiry farther.

In order to obtain direct evidence with regard to the position of the negative group in a case similar to that discussed above, we started in another experiment from the mono-bromine derivative of diethyl-benzene. This was readily made, though the lack of sufficient material made its purification impossible. It was oxidized with chromic acid and yielded a difficultly soluble acid. The barium and calcium salts also proved to be difficultly soluble. The acid, purified as far as possible, was mixed with an equal weight of quick-lime, and distilled in the hope that the corresponding brom-ethyl-benzene might be obtained, and that the oxidation of this with potassium permanganate would enable us to decide whether it was an ortho- or a meta-compound. The experiment was not successful. It will be repeated at the earliest opportunity. Experiments are now in progress with the object of determining whether an acid group can fully protect a residue as large as propyl from the oxidizing action of chromic acid.

JUNE, 1882.

[1] *Loc. cit.* [2] This Journal, **2**, 131.

ON THE OCCURRENCE OF A NEW FAT ACID IN THE NUT OF THE CALIFORNIA BAY TREE.

By J. M. Stillman and E. C. O'Neill.

The peculiar properties and composition of the essential oil of the California laurel or bay tree, *Umbellularia Californica* (otherwise known as *Oreodaphne Californica*, *Tetranthera Californica*, or *Laurus Californica*), as investigated by one of us,[1] made it seem of interest to investigate the fat occurring in the seed or nut of the tree. The tree in question is one of the most widely distributed as well as one of the largest and handsomest of the valley trees of California. It is evergreen; its wood is much used as an ornamental wood in cabinet-work. The leaves when crushed possess a powerful and penetrating odor, which, however, when not too strong is very pleasant. The same pleasant odor, but fainter, is present in the wood when freshly cut, even if the wood is seasoned.

The fruit consists of a berry something larger than the olive and of about the same shape, enclosing a smooth seed something smaller than an olive. This seed or nut has a thin but hard shell and a large dry kernel. The fruit grows abundantly at the proper season, December and January, and falls when ripe, at which time it can be easily gathered in large quantities. On the banks and in the beds of streams, where the tree seems to thrive best, we had no difficulty in collecting a water-bucket full of the fruit in about half an hour.

The nuts, divested of their fleshy husks and the shells, were thoroughly ground in a mortar, and then digested with pure ether in an apparatus which was essentially a modification of Drechsel's apparatus for the quantitative estimation of fats.[2] By this means, with little labor and a minimum quantity of ether, the entire amount of fat was readily extracted. The ether was then distilled, leaving the pure fat. By this process we obtained from one charge of 392 grams of nuts, 231.5 grams of fat, or a fat-content of 59 per cent. The fat thus obtained solidified on cooling to a hard tallowy mass, nearly white, melting at from 31° to 32° C., and of specific gravity 0.925 at 31° C. when melted. Its taste is disagreeable, producing in the throat irritation, possibly due to a certain quantity

[1] This Journal, **2**, 38.

[2] Journal für praktische Chemie, **15**, 1877, 350, plate II.

of free fat acid in the fat. The fat is readily soluble in ether and benzol, but very slightly in alcohol.

A considerable quantity of the fat was then saponified with strong caustic potash, and the resulting clear soap solution decomposed by dilute hydrochloric acid. The clear oily layer which separated on the surface was washed several times by shaking with hot water, separated and dried. On cooling it composed a white, dry, tallowy mass, of faint odor when cold, but when heated giving off a peculiarly disagreeable, irritating odor. Its taste is disagreeable, irritating the throat. Its melting point was found to vary from 31° to 34° C. with different preparations.

An analysis of the acid mass as thus set free, purified and dried, gave

C=71.24
H=11.91.

To ascertain whether the acid so prepared was homogeneous or composed of a mixture of acids, a fractional precipitation was undertaken. An alcoholic solution of the acid was treated with an alcoholic solution of magnesium acetate, the mixture saturated with ammonia and allowed to stand. Several successive fractions were removed in the course of a couple of days by filtration, of which the first fraction composed over one-fourth the entire mixture. The magnesium salts so obtained were decomposed, with hydrochloric acid, the fat acid washed repeatedly with hot water, and finally dissolved in alcohol and reprecipitated with water, and dried in the air-bath. The last two fractions separated, No. 6 and No. 7, were slightly brown, the others were white. The melting points of the fractions were as follows:

Fraction	1	2	3	4	5	6	7
Melting pt.	34°	34°	32°	31°	...	25°	21°

Presumably the fraction 1 would contain the acids of greatest molecular weight, and the last fractions those of lowest molecular weight. Hence elementary analyses of fractions 1 and 5 were undertaken, both of these being pure white, whereas 6 and 7 were slightly discolored. The results were as follows:

Fraction 1.

	I[1].	II.	III.	Calculated for $C_{11}H_{22}O_2$.
C	71.37	70.75	71.05	70.97
H	11.67	11.71	11.68	11.81

[1]This one analysis was made before complete purification of the fraction, and gave a slight ash on combustion.

Fraction 5.

C	71.04
H	11.74

A silver salt of the acid was prepared and analyzed.

	Found.	Calculated for $C_{11}H_{21}AgO_2$.
Ag	36.90	35.86

With one exception the analyses seemed to indicate a slightly high carbon content. We therefore decided to employ the method of Krafft,[1] by distillation under diminished pressure, to purify the acid. A quantity of the fat acid was first distilled under a diminished pressure of about 160 mm. of mercury. A large proportion passed over at from 240°–250° C., mostly in the neighborhood of 249°. A second portion was collected separately, which passed over at from 250°–270°, most of it passing over below 260°. The appearance of both portions of the distillate was pure white on cooling, and the lower fraction especially presented a distinct crystalline character. These fractions were then submitted to fractional distillation at ordinary atmospheric pressure. The distillation commenced at about 260° C., and small portions were left in the flask at 300°, the greater quantity passing over, however, between 265° and 275°, and this portion was again subjected to fractional distillation. The boiling point seemed to lie between 270°–275° (uncorrected, or corrected by Kopp's formula 275°–280°). This portion boiling from 265°–275° was again subjected to distillation in diminished pressure, and the first two-thirds of the distillate taken. The boiling point indicated by this last distillation under a diminished pressure of 100 mm. was about 205°–208° (or corrected by Kopp's formula 208°–211°).

The melting points of the fractions obtained by the distillation under ordinary atmospheric pressure varied from 21° for the lowest fraction to 38° for the residue remaining in the flask; those portions of the distillate of most clearly crystalline character and most nearly constant boiling point melted at from 21° to 23°. To obtain a more accurate melting point we took:

(*a*) The fraction distilling from 270°–272° and melting at 21°, purified it by solution in alcohol and reprecipitation by water, and dried it at 110°. It then melted at 21.2°.

[1] Berichte der deutschen chemischen Gesellschaft, **11**, 2219.

(*b*) A portion distilling at 272°–275° and melting at 22°. This was converted into a silver salt, and the acid set free from the silver salt by dilute nitric acid, and the acid thus set free was purified as above. It melted at 22.5°–22.8°.

(*c*) A portion of the last-mentioned distillate under diminished pressure. This melted at 21.2°.

In order to check the composition of these fractions, analyses of silver salts prepared from them and recrystallized from hot alcohol, were made. As the silver salts were reduced by boiling alcohol, we had some difficulty in getting specimens which, on drying from the alcohol, would not turn brown in the drying.

The silver salt prepared from (*a*) gave 36.40 per cent. Ag; calculated for $C_{11}H_{21}AgO_2 = 36.86$. This result was a little low, but the salt dried partially on the filter-paper and a few shreds of the filter-paper adhered to it, which is perhaps sufficient to account for the low result, the salt being small in quantity.

The silver salt of (*b*) gave Ag = 36.77 per cent.; (salt pure white when dry).

The silver salt of (*c*) gave

I. Ag = 37.06 (nearly pure white when dry).

II. Ag = 37.21 (brown on the edges when dry).

A silver salt was prepared from the residues remaining in the flask after the distillation under diminished pressure. Its analysis gave Ag = 34.17 per cent., showing a probable admixture of some higher acid or acids in the higher boiling fractions.[1]

Ethers.

The methyl ether was prepared by acting on a solution of the fat acid (as set free from the fat) in methyl alcohol, with dry hydrochloric acid. The liquid soon separated into two layers. When saturation was complete the flask was warmed on the sand-bath to expel the excess of alcohol and acid, the remaining liquid washed with water and dried over calcium chloride. The ether distilled over mainly from 240° to 250° C., and on the third fractional distillation indicated a boiling point of 244° to 246°; it constitutes a mobile liquid of pleasant odor.

[1] Elementary analyses of the fraction denominated (*c*) above were attempted, but, owing to the quality of the gasoline in use at the time, it was found impossible to heat the combustion tube to a sufficient temperature, and the results were not accordant. The analysis made under most favorable circumstances in this respect gave C = 70.55; H = 11.61.

The ethyl ether was obtained in the same way by the use of absolute alcohol. On a third fractional distillation it passed over mainly from 248° to 258°, its boiling point apparently lying between 253° and 255°. A portion passing over at this latter temperature was subjected to elementary analysis.

Found.	Calculated for $C_{11}H_{21}(C_2H_5)O_2$
C 72.83	C 72.90
H 12.15	H 12.15

This also was a mobile colorless liquid of pleasant odor.

The amyl ether, prepared in a similar way from amyl alcohol, is also capable of distillation with but slight decomposition, boiling at about 295° C. It is a mobile liquid of agreeable odor.

It will appear evident, we think, from the above data, that a new acid of the acetic acid series constitutes the main portion of the fat under investigation. The designation which it seems most appropriate to apply to this acid is that taken from the now accepted name of the tree, viz. *Umbellulic acid.* There seems to be present, however, a certain quantity of some higher acid, possibly also a small quantity of some lower acid. The umbellulic acid is a white crystalline solid of peculiar taste, irritating the mucous membrane of the throat. This peculiar taste was noticed in the acid after distillation, after purification with alcohol and water, and also in the acid obtained from the decomposition of the silver salts. It does not seem probable, therefore, that the taste is due to mere impurities. The same taste is noticed in the fresh nut as well. The acid distills at ordinary atmospheric pressure without decomposition, giving a water-clear distillate, which solidifies on cooling to a white crystalline solid. Its melting point seems to be from 21° to 23° C., but small quantities of other acids perhaps raise the melting point appreciably above these figures. The boiling point, as noticed above, appears to be at from 275° to 280° (corrected according to Kopp's formula) at ordinary pressure, and at 208°–211° under a pressure of 100 mm. The undecylic acid of Krafft[1] boils at 212.6° at 100 mm., and its melting point is 28.5°, but apparently it does not distil at ordinary pressure without decomposition. Other data for comparison are wanting. The results of this investigation are the more remarkable inasmuch as they are not in accordance with the general theory that the natural fats

[1] Berichte der deutschen chemischen Gesellschaft, **11**, 2219; **12**, 1667.

contain only acids with an even number of carbon atoms in the molecule, although the occurrence of inactive valerianic acid in dolphin oil[1] would be at least one exception to that rule, and others have been noticed, which demand further confirmation, however. Until some causal connection between the occurrence in natural fats and the even number of carbon atoms has been established, too much reliance should not be placed on the general rule.

If opportunity offers we shall endeavor, during the next university year, to resume the study of this interesting acid and its derivatives.

Laboratory of the University of California, BERKELEY, *May* 10, 1882.

Contributions from the Chemical Laboratory of Rutgers College.

VI.—ON THE PRECIPITATION OF TITANIC ACID.

BY PETER T. AUSTEN AND F. A. WILBER.

In the analysis of titaniferous ores by fusion with the carbonates and nitrates of the alkalies, the fused mass is soaked out with water, the solution acidified with chlorhydric acid, evaporated to dryness to render the silica insoluble, then taken up with chlorhydric acid and water, and filtered. In the residue consisting of silica, containing more or less ferric oxide, titanic acid and phosphoric acid, the silicic acid is determined by expulsion with fluohydric acid. The residue consisting of titanic acid, ferric oxide and phosphoric acid is then fused with an alkaline bisulphate and the resulting solution added to the chlorhydric acid solution, which has been freed from platinum by treatment with hydrogen sulphide.

To determine the titanic acid in this chlorhydric acid solution it is necessary to precipitate an aliquot part of it with an excess of potassium hydrate (first oxidizing the ferrous salts by potassium

[1] Chevreul, cited in Roscoe and Schorlemmer's Chemistry, **3**, I, 618.

chlorate), filter off and wash the bulky gelatinous precipitate of ferric oxide, titanic acid, phosphates, etc., dissolve the mass in sulphuric acid, reduce and precipitate the titanic acid by boiling. It is not practicable to precipitate the titanic acid directly by boiling the chlorhydric acid solution, since the precipitation by this method is not complete, and when thus precipitated it runs through the filter-paper as soon as the wash-water ceases to be acid. If the wash-water is acidified with chlorhydric acid, the precipitate is more or less dissolved.[1] The filtration and washing of this precipitate is extremely irksome, and, like that of the basic acetates, is seldom really perfect.

On the other hand the method of decomposing the ores with an alkaline bisulphate, which yields at once a sulphuric acid solution, is often very tedious, on account of the stability of many ores toward this flux and the length of time that it frequently takes to remove the fused mass from the crucible, especially when potassium bisulphate has been used and the temperature has been too high, or not enough sulphuric acid has been added at the close. There are but few ores which are not decomposed by the alkaline carbonates and nitrates when the fusion is finished in a small Fletcher injection furnace, and if rightly handled during cooling the fusion will come out of the crucible in a few hours.

The results obtained by Streit and Franz[2] do not seem to have been utilized in the analysis of titaniferous iron ores. According to these authors, titanic acid may be precipitated from its chlorhydric acid solution in a form which can be easily filtered and washed, when to the solution one-third of its volume of sulphuric acid (containing one-sixth volume of H_2SO_4) and one-fifth of its volume of acetic acid are added. In using this method, however, we have found that when considerable amounts of chlorhydric acid were present, the addition of so much sulphuric acid prevented the precipitation of the titanic acid.

If also it is the intention to determine manganese by the beautiful oxalate method of Classen[3] which does away with the tedious basic acetate procedure, it is of importance that but a small amount of sulphates should be present.[4] We were led, therefore, to experiment on the precipitation of titanic acid from its chlorhydric acid solution by the addition of acetic acid alone, and find that it answers the

[1] Rose, Quant. Anal. 1871, **2**, 313.
[2] J. pr. Chem. **108**, 65.
[3] Fres. Zeit. **18**, 175.
[4] Fres. Zeit. **18**, 186.

purpose in every way as well, if not better, than when a mixture of acetic and sulphuric acids is employed. The titanic acid is precipitated from its reduced solution on boiling as a flocculent precipitate which settles rapidly and well. The hot solution can be easily filtered without waiting for it to settle. The precipitate shows no tendency to run through the paper if washed with hot water acidified with acetic acid. In fact the addition of a little acetic acid to the wash-water, in cases where the titanic acid, precipitated by the usual method, shows a tendency to run through, stops it at once. The titanic acid when precipitated in the presence of acetic acid, from a chlorhydric solution containing ferrous salts of iron, is as free from iron as when precipitated by the usual method. It is rare that a precipitate of titanic acid is obtained perfectly free from iron in actual analysis when the solution contains a considerable amount of iron. In the presence of phosphates it always contains iron and phosphoric acid,[1] and has to be worked over again.

A number of experiments were made with titaniferous ores to ascertain if the precipitation of titanic acid from a chlorhydric solution in the presence of acetic acid was complete. In no case could the slightest trace of titanic acid be detected in the filtrates by means of tin and chlorhydric acid.

There are, of course, many modifications possible in the analysis of titaniferous ores, and various applications can be made of this method of precipitating titanium, but the following course seems to offer some advantages.

The ore is fused with alkaline carbonates and nitrates, and after taking up with water in the usual manner, is acidified with chlorhydric acid and evaporated to dryness to render the silica insoluble. It is then moistened with chlorhydric acid and treated with a little warm water till solution of the soluble parts has been effected, after which it is allowed to cool, and then diluted, without filtering, to 400–500 cc. Sulphurous acid is next added, and then 50–60 cc. of acetic acid. On boiling in the usual manner, the titanic acid will be precipitated in a flocculent and easily filterable state. The whole is then filtered and washed with hot water containing a little acetic acid. If the ore does not contain phosphoric acid this precipitate will be quite free from iron, and after expelling the silica by treatment with ammonium fluoride and sulphuric acid is generally pure enough to be taken as titanic acid, although in cer-

[1] Bogardus, Am. J. Sci. **3**, 8, 334.

tain cases where the amount of titanic acid is small and the amount of iron large, a re-fusion is often necessary. In case the ore contains phosphates, the titanic acid precipitate will always contain iron and phosphoric acid. In this case, the residue, after expelling the silica with ammonium fluoride, can be fused with sodium carbonate and the fusion extracted with water, which dissolves the sodium phosphate and leaves the sodium titanate and ferric oxides.[1] This residue is then fused with a little sodium bisulphate, and the titanic acid precipitated after reduction by boiling. The filtrate containing the iron which was precipitated with the silica is now added to the filtrate from the original precipitation of the titanic acid, and the acidified filtrate from the fusion of the titanic acid with sodium carbonate,[2] and the united solutions analyzed for alumina, iron, manganese, calcium and magnesia, after freeing it from platinum by precipitation with hydrogen sulphide.

NEW BRUNSWICK, N. J.

REVIEWS AND REPORTS.

REPORT ON PROGRESS IN PHYSIOLOGICAL CHEMISTRY.

[*Continued from Vol.* 3, 450.]

GASTRIC DIGESTION AND THE PRODUCTS FORMED.

Digestion in the Stomach and Intestines.—Nearly all our knowledge in regard to the chemistry of the digestive process is based upon experiments on artificial digestions carried on outside the animal body. Recently, however, Schmidt-Mülheim[3] under the guidance of C. Ludwig, of Leipzig, has undertaken a methodical examination of the alterations which proteid bodies undergo in the alimentary canal, studying for this purpose the normal process as carried on in the digestive apparatus of dogs. The animals employed were as nearly alike as possible in weight, race and temperament, and prior to the experiment were kept for two days entirely without food, in order to have the digestive apparatus freed as far

[1] Drown and Shimer, this Journal, **4**, 6.
[2] This is hardly necessary unless phosphoric acid is to be determined in this solution.
[3] Du Bois Reymond's Archiv. f. Physiolog. 1879, 39.

as possible from all traces of previous food. The proteid material employed was horse-flesh, which, after being freed from fat and collagenous tissue, was finely divided and boiled with water for fifteen minutes for the complete removal of all crystalline constituents such as creatin, etc. The content of albumin in the so prepared food was calculated from a determination of nitrogen made according to the method of Dumas.

In carrying out the experiments each dog received 200 grams of flesh, and after the lapse of a definite time the animal was killed by the injection of potassium cyanide into the thorax. The abdomen was then immediately opened and the contents of the stomach and intestines were separated by two ligatures placed at the commencement of the duodenum. The contents of the two were then removed separately, and the walls of the canal were freed from any adhering matter by thorough washing with water. The undigested portion was collected by filtration, and after thorough washing with water was dried, and from a determination of its nitrogen the quantity of undissolved albumin was calculated.

In order to determine the dissolved albumin a measured quantity of the filtered fluid was mixed with ferrous acetate and a small quantity of ferrous sulphate, and then boiled. The brown flocculent precipitate was then carefully collected, washed and dried at 100° C. Its content of nitrogen was determined by the method of Dumas, and from the data so obtained the amount of soluble albumin was calculated; 15.6 per cent. being considered the average amount of nitrogen present in albumin. To separate the peptones the united filtrate and wash-water from the albumin precipitate were concentrated to a small bulk, and when cold the fluid was made strongly acid with acetic acid, and then phosphotungstic acid was added until a filtered portion of the solution failed to give even the faintest red color with cupric sulphate and sodium hydroxide. The white tungstic acid precipitate was treated in the same manner as the iron precipitate, and from the content of nitrogen the amount of peptones was calculated, using the same factor as before. The crystalline decomposition products were looked for in the albumin and peptone free solution from the intestines. The method consisted in evaporating the filtrates to dryness and dividing the residue into three portions: for the leucin one portion was extracted with hot alcohol, and in this concentrated extract the easily identified crystals of leucin were sought for; for the detection of tyrosin another portion of the residue was examined by Piria's method; finally, in the third portion of the residue nitrogen was determined, from which the total amount of crystalline decomposition products of the albumin was calculated; in this latter case, however, the results are undoubtedly too high, from the presence of portions of nitrogenous constituents of bile. Following are the results obtained in five experiments:

	1 hour after feeding.	4 hours after feeding.	6 hours after feeding.	9 hours after feeding.	12 hours after feeding.
Soluble albumin in stomach,	2.262 grams	2.086 grams	2.096 grams	1.810 grams	0.049 grams
Peptone in stomach,	3.087 "	3.312 "	2.912 "	3.422 "	0.083 "
Unaltered food in stomach,	50.389 "	25.928 "	17.833 "	7.077 "	0.120 "
Dissolved albumin in intestines,	0.482 "	0.436 "	0.917 "	0.438 "	0.202 "
Peptones in intestines,	0.512 "	0.498 "	1.352 "	1.222 "	0.820 "
Undissolved matter in intestines,	1.914 "	1.912 "	2.743 "	1.840 "	1.936 "
	58.746 "	34.622 "	27.853 "	15.329 "	3.210 "
Albumin fed,	61.150 "	65.817 "	64.000 "	62.013 "	61.705 "
Albumin absorbed,	2.404 "	31.195 "	36.147 "	46.684 "	58.515 "

Leucin and tyrosin were found only in the merest traces.

From these results it is clearly seen that a much longer time is needed for the completion of the digestive process than has hitherto been supposed. Even after nine hours' digestion, unaltered food is still found in the stomach, and food too which from its finely divided condition and by boiling has been changed to the easiest state of digestibility possible. Only after twelve hours can the digestion be considered as finished. The following table clearly shows several other points connected with digestion in the stomach which are worthy of notice.

Time after feeding,	Proportion of dissolved albumin to peptones.	Quantity of dissolved albumin aad peptones.	Weight of peptones.
1 hour	1 : 1.4	5.349 grams	3.087 grams
2 hours	1 : 2.0	5.448 "	3.653 "
4 "	1 : 1.6	5.398 "	3.312 "
6 "	1 : 1.4	5.008 "	2.912 "
9 "	1 : 1.8	5.052 "	3.242 "
12 "	1 : 1.8	... "	... "

It is thus very apparent that among the products formed in gastric digestion, the peptones at all times in the process exceed in amount the dissolved albumin; also that the relative proportion of these two proteids is not materially altered in the different stages of digestion. Again, it is to be noticed that the total quantity of dissolved albumin and peptones present in the stomach is practically the same at all times during the digestion, and also that the quantity of peptones varies only slightly. These facts would seem to indicate that after the formation of a definite quantity of the digestive products, the transportation of these bodies keeps pace with the digestion, so that at no time can there be an accumulation of the digestive products. Mülheim is of the opinion, from the composition of the contents of the intestinal canal, that a not inconsiderable portion of the soluble contents of the stomach passes on into the intestines, instead of being at once absorbed from the stomach.

In the intestinal digestion Mülheim found in all his experiments that the contents of the small intestines possessed an acid reaction; this was the case not only with the fluid contents of the upper end of the small intestines, but also with the brown and more solid mass at the lower end. This result, which is contradictory to the prevalent idea that the three alkaline digestive fluids, bile, pancreatic and intestinal juices, are sufficiently strong to render the entire contents of the intestinal canal at once alkaline, has an important bearing on pancreatic digestion. While in alkaline digestive fluids putrefaction soon shows itself with simultaneous formation of crystalline decomposition products together with large quantities of indol, the digestion of albumin by an acid pancreatic juice is more analogous to a pure digestive process. Again, Mülheim remarks that the acid reaction is a necessity for the formation of the viscous yellow precipitate which is found in the small intestines; which precipitate Mülheim is inclined to think is of great importance to pepsin digestion. Calling attention to Brücke's statement that pepsin possesses the property in the highest degree of attaching itself to small particles, he reasons that the bile precipitate serves the purpose of holding temporarily the pepsin, so as to prevent the destruction of the trypsin, which according to Kühne is digested by pepsin in acid solution, the ferment being liberated again when the bile precipitate is dissolved in consequence of the ultimate alkaline reaction, which usually appears at the end of the small intestines. Thus it is the rôle of the precipitate to prevent the destruction of the pancreatic ferment by the gastric juice in the small intestines. Further on, where the fluids are alkaline, the pepsin is powerless, being inactive in an alkaline medium.

Again, the amounts of crystalline proteid decomposition products found in the intestinal canal under the physiological conditions described, are so unimportant it would appear that only an inappreciable quantity of albumin is absorbed in the form of crystalline products in normal digestion.

Absorption of Albumin in the Stomach.—Relative to the absorption of albumin in the stomach, Dr. v. Anrep[1] has experimented with dogs, introducing into the stomach by means of a stomach fistula a definite amount of syntonin in solution. The pyloric opening of the duodenum was closed, and prior to the experiment the animal was deprived of food for 24 hours, while just before the albumin solution was introduced the stomach was thoroughly rinsed with water. The solution of albumin was introduced into the stomach by the fistula, which was then stoppered. After a definite time the contents of the stomach were emptied into a dish, and in the fluid the amounts of syntonin and peptones were determined by analysis. The following table shows the results:

[1] Die Aufsaugung im Magen des Hundes. Du Bois Reymond's Archiv. 1881, 504.

Am't of substance introduced.	Am't found in stomach. Syntonin.	Peptone.	Quantity absorbed.	Per cent. of absorbed albumin.	Length of time.
4.2 grams syntonin,	0.327 gram	2.898 grams	0.975 gram	23.3 per cent.	1 hr. 30 min.
12.79 " "	6.534 "	2.688 "	3.537 "	27.9 "	1 " 40 "
2.124[1] " "	0	0.729 "	1.397 "	65.6 "	1 " 40 "
5.91 " peptone,	..	3.099 "	1.872 "	31.7 "	1 " 45 "
12.25 " "	..	8.103 "	4.847 "	33.9 "	1 " 45 "

It would thus appear from Dr. v. Anrep's experiments that the stomach possesses the power of absorbing peptones, though as to the relative absorption by the stomach and intestines little is shown.

Decomposition of neutral Fats in the living Stomach.—Dr. Ogata,[2] by the use of methods similar to those employed by Dr. v. Anrep, has studied the behavior of neutral fats in the living stomach of dogs. Prior to the experiment the stomach of the fasting animal was thorough rinsed, through the fistula, with .5 per cent. salt solution; 50–60 cc. of perfectly neutral olein were then introduced into the stomach, remaining there from two and a half to three hours. At the end of this time Dr. Ogata succeeded in four cases in finding clear evidence of the presence of oleic acid.

R. H. CHITTENDEN.

(*To be continued.*)

RECENT PROGRESS IN AGRICULTURAL SCIENCE.

[*Continued from p.* 152.]

In regard to the sources of *nitrogen* to the plant, little that is new has been reported. Ad. Mayer[3] has reinvestigated the question of the assimilability of ammonia by the leaves of plants. He finds that the higher plants are capable of taking up ammonium carbonate through their leaves, both when it is dissolved in water and when it is in the gaseous state; and that the process is not simply a mechanical one, but that the nitrogen thus introduced into the plant is assimilated. Too great concentration of the ammonium carbonate is fatal to the life of the plant, but small amounts were found to be harmless and to exert no effect on the respiration of the plant. In view of the fact that leguminous plants are popularly believed to gather considerable quantities of nitrogen from the air, trials were made with these plants, but they were not found to have any peculiar power in this respect. As to the practical significance of this capacity of vegetation to assimilate nitrogen through its leaves, Mayer comes to the conclusion that it is very small.

[1] This experiment yields too high results, owing to an incomplete washing out of the stomach.
[2] Du Bois Reymond's Archiv. 1881, 515. [3] Jahresber. agr. Chem. 16-17 1, 286.

Experiments by Hässelbarth[1] and Wein,[2] on the relative value of nitrates and ammonia as plant food, gave the same results as most previous experiments on this subject, viz. that, while nitrates are readily assimilated, ammonia is taken up with difficulty, if at all. Hässelbarth experimented on barley, growing it in purified quartz sand watered with solutions of plant food. The normal solution contained

2 mg. equivalents		KH_2PO_4
1 "	"	KCl
1.6 "	"	$MgSO_4$
5 "	"	$Fe_2(HO)_6$
16 "	"	$Ca(NO_3)_2$

The ferric hydrate was mixed with the sand and the remaining substances given in solution. In four other experiments the same amount of nitrogen was supplied respectively as ammonium sulphate, phosphate [$NH_4H_2PO_4$], chloride and nitrate, while the calcium was supplied as sulphate. In a second series of experiments the same mixtures were used, but with the addition of 40 grams of $CaCO_3$ to each pot, while a third series was added precisely like the second, except that no plants were introduced, the pots serving to test the amount of nitrification taking place. At the close of the experiments the total dry matter, nitrogen, and lime of the plants (exclusive of roots) were determined. It was found that nearly the total amount of nitrogen present as nitrates was assimilated, as was also that of the ammonium sulphate and chloride *in the presence of* $CaCO_3$. In those cases in which no $CaCO_3$ was present, only about half the nitrogen of the last named salts was assimilated, and only about one-third as much dry matter was produced as in the other cases. The ammonium phosphate seemed to be the least adapted to the barley plant of any of the salts tried, only about three-fifths of its nitrogen being assimilated in the presence of $CaCO_3$, and only about one-seventh in its absence, while the amount of dry matter in the latter case was even less than that produced when no nitrogen whatever was added to the soil. Hässelbarth believes that the better results obtained in the presence of $CaCO_3$ are due to the nitrification of the ammonium salts, favored by the presence of the calcium carbonate, and in fact in his control pots from 36 to 52 per cent. of the nitrogen was converted from ammonia to nitric acid during the time of the experiments. Another explanation of the favorable action of $CaCO_3$ is, however, possible. It is a well-established fact that, when salts of ammonium are offered to the roots of a growing plant, the base is taken up more rapidly than the acid, thus leaving the solution acid, and that if the process continues the acidity may soon become such as to injure or destroy the plant. Hässelbarth makes no mention of any precautions having been taken to pre-

[1] Landw. Versuchs-Stationen, **21**, 363. [2] Jahresber. agr. Chem. N. F. **2**, 190.

vent this action in his experiments, and it is quite conceivable that the $CaCO_3$ was of benefit simply by neutralizing the acid set free from the ammonium salts and thus preventing it from injuring the plant. This is perhaps also indicated by the fact that the plants in the pots containing $CaCO_3$ assimilated more lime than any of the others, even those fed with calcium nitrate. If the action of the calcium carbonate was such as we have supposed, it is evident that the plants had presented to them an extra quantity of soluble lime salts, some of which would probably be taken up. While, then, it is probable that nitrification explains part at least of the good effects of the $CaCO_3$ in these experiments, the results are not conclusive against an assimilation of ammonia.

Wein's experiments were very similar to those of Hässelbarth, except that he used artificial humus instead of sand, and cultivated several kinds of plants, including oats, peas and soja beans. His results appear to have also been much the same, but in the experiments with ammonium sulphate a renewed growth was noticed toward the end of the experiment, as in Beyer's well-known experiment, and apparently from the same cause, viz. nitrification of the ammonia.

Wein's experiments were suggested by the previous experiments of Lehmann[1] on the same subject, and Hässelbarth's results are of interest in the same connection. Lehmann's most striking results were obtained with maize by the method of water culture. On attempting to grow young maize plants in solutions identical as regards mineral matters, but furnishing nitrogen respectively as calcium nitrate and ammonium sulphate, the plants of the ammonia series grew luxuriantly at first, while those of the nitric acid series showed all the signs of deficient nutrition. After about forty-one days, however, a sudden change was observed. The plants of the nitric acid series became of a healthy green, and from this time on grew rapidly and normally, while the plants of the ammonia series, on the other hand, lost their healthy color, became sickly, and remained so during the rest of the experiment, falling much below the nitric acid plants in the amount of crop.

On removing sickly plants of the ammonia series into solutions containing nitrates they promptly recovered and grew normally, while healthy plants of the nitric acid series, when removed into solutions containing only ammoniacal nitrogen, speedily took on the sickly character of the plants raised in such solutions. In the same way, in the earlier stages of the experiment, the sickly plants of the nitric acid series recovered within two days when placed in the ammonia solution, while the ammonia plants became sickly when placed in the nitrate solution.

Similar, but not quite so decided, results were obtained with tobacco plants cultivated in sand.

Lehmann concludes that these two plants in their early stages of growth require their nitrogen to be presented in the form of

[1] Biedermann's Central-Blatt. Jahrg. 4, 403.

ammonia, while in later stages of development they can assimilate it only from nitrates. Buckwheat and yellow lupines, on the contrary, he found to require nitrates throughout their whole period of growth.

If we accept Lehmann's results as correct, then Hässelbarth's and Wein's experiments indicate that the plants which they experimented upon belong to the class of "nitric acid plants," *i. e.* plants which require nitrates throughout their growth; and in manuring them we should either use fertilizers containing nitrates or apply our nitrogenous fertilizers sufficiently long beforehand to permit their nitrification in the soil to begin at least.

Lehmann's results, or rather the conclusions which he draws from them, seem, however, to be somewhat questionable. Hampe,[1] in 1867, produced a maize plant 2½ feet high, bearing 40 seeds, in a solution intended and asserted to contain no nitrates. At a certain stage of growth the plants showed signs of disturbed nutrition, but recovered in a week or two. Hampe's conclusion is that "the plants, while young, were unable to assimilate ammonia or did so with difficulty, but acquired the power with a certain age." Wagner,[2] in 1868, obtained exactly the same results as Hampe. These results appear to be directly opposed to Lehmann's, but still, in view of the readiness with which, as we now know, ammonium salts are nitrified in dilute solutions, too much weight is not to be attached to them. It is possible that the renewed growth in Hampe's experiments was due to the formation of nitrates in the solution.

A more weighty argument against Lehmann's theory is the fact that luxuriant maize plants have been raised in solutions containing from the start no nitrogen except in the form of nitrates. Knop,[3] for example, produced a maize plant having a dry weight of over 50 grams, or a green weight of 330 grams, and bearing an ear containing 140 ripe seeds, in a solution containing the nitrates of potassium and calcium as sole sources of nitrogen. Knop also recommends a solution containing nitrate and phosphate of potassium, nitrate of calcium, sulphate of magnesium, and a little phosphate of iron, as well adapted to water-culture experiments, although he does not mention maize in particular; and in the very numerous experiments with other plants which have been made, nitrates have invariably proved a sufficient source of nitrogen. While, then, it would hardly be safe to reject Lehmann's results, they certainly require confirmation before they are accepted.

The most noticeable recent experiments on the sources of the *ash ingredients* of plants are those of Grandeau,[4] on the functions of the so-called *matière noir* of fertile soils, by which term he designates the black organic matter, insoluble in water or acids, but soluble in alkalies, which can be extracted from the soil by

[1] Johnson "How Crops Feed," 303. [2] *Ibid.* 304.
[3] Kreislauf des Stoffs, 2, 239.
[4] Annales de la Station Agronomique de l'Est, 1878, 225-352.

ammonia. We have already seen that the organic matter of the soil does not, in all probability, contribute directly to the growth of the plant to any appreciable extent. Notwithstanding this, however, it is a well-known fact that in general those soils which are distinguished for their fertility contain much humus, and that the addition of organic matter to soils deficient in it usually improves them. In Grandeau's opinion, the effect of the organic matter on the physical character of the soil is not a sufficient explanation of its action, and his hypothesis in regard to the rôle of the *matière noir*, the result of much study and experiment, attributes its chief value to a peculiar chemical action between it and the inorganic matters of the soil. While not denying that the roots of plants may extract nourishment from the solid particles of the soil, he holds that no *agriculturally profitable* production can take place unless some substance is present in the soil which can dissolve the comparatively insoluble mineral food which it contains and present it to the plant in a more assimilable form. To do this is the office of his *matière noir*. It is not itself assimilated by plants, but it unites with the inorganic plant food present in the soil to form a peculiar compound, from which the plant takes the potash, phosphoric acid, etc., which it needs, leaving the organic residue to take up a fresh portion of these substances from the soil. That is, the *matière noir* serves as a carrier of plant food between the soil and the plant, in a manner analogous to the action of the oxides of nitrogen in the manufacture of sulphuric acid. To extract this *matière noir* from the soil, Grandeau proceeds as follows: The soil is first treated with very dilute hydrochloric acid to decompose the insoluble lime compound in which the *matière noir* exists in the soil. The acid is washed out with water, and on then treating the soil with ammonia, a solution of the *matière noir* is obtained, which, on evaporation, deposits the substance as a shining, carbonaceous mass. The substance thus obtained contains, besides organic matter, a greater or less amount of ash, composed to a considerable extent of silica, but containing also all the mineral nutrients of the plant, the predominant ingredients, after silica, being the phosphates of iron and alumina. Analyses of the ash of *matière noir* have been made by Grandeau, and also by Pitsch. Grandeau's results were:

Silica,	35.60
Oxide of iron (combined with silica),	18.36
Oxide of manganese (combined with silica),	0.18
Lime (combined with silica),	3.55
Tribasic phosphate of lime,	2.66
Phosphate of iron,	34.41
Magnesia,	1.28
Potash,	3.94
	99.98

Pitsch obtained the following figures:

	Clay Soil.	Sandy Soil.
Chlorine,	0.07	trace
Char.	6.00	0.08
Silica,	33.70	17.19
Iron oxide,	17.03	24.39
Alumina,	3.40	5.50
Phosphoric acid,	29.94	38.10
Manganese,	1.04	5.73
Lime,	2.35	1.68
Magnesia,	3.53	1.64
Potash,	7.30	4.06
Soda,	3.08	0.13
Sulphuric acid,	trace	0.16
	107.44	98.66

In the ammoniacal solution of the *matière noir*, according to Grandeau, the mineral matters cannot be detected by the ordinary reagents, and he therefore assumes the existence of a peculiar chemical compound between them and the organic matter, which is the means of supplying the plant with its ash ingredients in the manner described. The facts on which Grandeau bases his hypothesis are substantially the following:

1st. In a large number of soils examined by him, the actual fertility, as shown by experience, was found to correspond quite closely with the amount of *matière noir* extracted from them by ammonia, and still more closely with the amount of ash ingredients contained in the latter, while neither the total organic matter nor the amount of mineral matter extractable by acids showed such a relation.

2d. On subjecting a solution of *matière noir* to dialysis, the mineral matters passed readily through the membrane while the organic matter remained behind. Since the solution contained all the essential ash ingredients, its capacity to nourish plants was thus shown. Plants were also grown successfully in sterile sand watered with a solution of *matière noir*. At the close of the experiment the roots were found covered with black, flocculent organic matter containing very little ash. No trace of the organic matter having entered the roots could be perceived. The solution, which was at first alkaline, assumed an acid reaction in the pots and became decolorized.

3d. To show the necessity of the *matière noir* for the growth of plants, a kilogramme of Russian "black earth" was halved. From one-half the *matière noir* was extracted, while the other half was left in its natural state, and in each half a bean plant was grown. That in the original soil grew normally, while that in the extracted soil grew very feebly and produced only a few early withering leaves.

Experiments were also made as follows: Four boxes of soil, having one square meter of surface each, which had been treated exactly alike in two successive vegetation experiments, were used. Two of them contained a calcareous soil, the other two a clay soil. From one box of each pair the soil was removed to the depth of 20 cm., mixed with an equal weight of a sterile peat, and the mixture replaced in the box. On the next day the soil of the other two boxes was cultivated to the depth of 20 cm., and all four boxes were manured with 100 grams of dicalcic phosphate. Eleven days afterward the soil was again cultivated and 30 grams of chevallier barley sown in each box. The crop of grain in each box was:

I.	Calcareous soil	without	peat,	430	grams.
II.	"	" with	"	800	"
III.	Clay	" without	"	600	"
IV.	"	" with	"	775	"

To show that these differences were really due to the *matière noir*, Grandeau gives the following table:

	100 grams soil contained of *matière noir*.	The *matière noir* of 100 grams soil contained of P_2O_5.	Crop.
Box I.	0.98 gram.	0.03 gram.	430 grams.
" II.	1.14 "	0.10 "	800 "
" III.	1.20 "	0.06 "	600 "
" IV.	2.22 "	0.08 "	775 "

The favorable action of the peat continued to show itself through several subsequent years, and imparted to the soils superior physical properties.

In considering Grandeau's theory of the rôle of the organic matter of the soil, two distinct questions present themselves: first, does the amount of plant food extracted from a soil by dilute ammonia furnish an appropriate indication of its fertility; and second, if this is the case, are Grandeau's views as to the manner in which the humus of the soil contributes to the nutrition of plants correct? The answer to the first of these questions is to be found by the statistical method; by the examination of a large number of soils whose crop-producing power is known. Such examinations have been made by Grandeau himself on thirty soils, by Pitsch[1] on fifteen soils, and by Tuxen[2] on five soils.

Grandeau determined the total amount of organic matter in his soils, the amount of organic matter soluble in dilute ammonia after treatment with dilute acid, and in the latter the total ash and the phosphoric acid, the latter ingredient being regarded as one of the most important. It was found that the fertility of these soils was in general proportional to the amount of *matière noir* which

[1] Landw. Versuchs-Stationen, **26**, 1. [2] *Ibid.* **26**, 114.

they contained, and more closely proportional to the amount of phosphoric acid which the latter contained. The fifteen soils examined by Pitsch also gave the same result.

Tuxen experimented on a sample of soil from the Nile valley, a sample of leaf mould, and three samples of a clay soil from near Copenhagen. The last three samples were of the same soil, but had received different treatment, one not having been manured for 21 years, one having received only mineral fertilizers for 17 years, and the third having been heavily manured with stable manure for 17 years.

The Nile soil, in spite of its great fertility, stood next to the last as regards the amount of phosphoric acid extracted. The other soils stood about in the order of their fertility in this respect, but the differences were comparatively small, and in Tuxen's opinion too small to account for the differences in fertility. The amount of ash ingredients extracted by the preliminary treatment with dilute acid seemed to correspond more closely with the actual fertility.

In three of the samples examined by Pitsch, the preliminary treatment with dilute acid also removed a large proportion of the phosphoric acid, so that very little was left for the ammonia to remove. In these cases Pitsch adds the P_2O_5 extracted by dilute acid to that found in the *matière noir*, and thus brings his results into harmony with Grandeau's. If we pursue the same course with Tuxen's soils, the results agree better with the observed fertility, though the two are by no means numerically proportional.

On the whole it would appear from the experiments thus far made that the amount of mineral matters, particularly of phosphoric acid, extracted from a soil by ammonia after previous treatment with dilute acid, may aid essentially in forming a judgment as to its fertility. It will be noticed that the most unfavorable results were obtained on clay soils.

Admitting, now, that the determination of the matters extracted by ammonia affords an approximate measure of the fertility of a soil, are Grandeau's views as to the peculiar functions of the *matière noir* correct? That the humus of the soil is *useful* is denied by no one, but is it *essential?*

In the first place it is to be remarked that the *matière noir* exists in the soil in an *insoluble* form; a fact admitted by Grandeau, since he employs a preliminary treatment with dilute acid, as he expressly states, to set it free from its insoluble lime and magnesia compounds.

This fact, however, deprives all Grandeau's experiments on the diffusibility of the ash ingredients of his *matière noir* and on the nutrition of plants by means of a solution of it, and all his theories as to its action in presenting plant food to the roots of the plant in a soluble form, of all value in this regard. If the *matière noir* exists in an insoluble compound in the soil, it may furnish food to the plant, but it does not present it in a soluble form, unless indeed

we are to suppose that the roots first excrete an acid and then an alkali.

It is of course conceivable, however, that the *matière noir*, although insoluble, may still be an important source of plant food, since it is well known that the roots of plants exert a considerable solvent action on the ingredients of the soil.

What, then, are the proofs which Grandeau brings forward of the existence of a peculiar compound of organic and inorganic matter which is the only source from which agricultural plants can derive food in sufficient quantity to render their cultivation profitable?

First he calls attention to the properties of the matter extracted from the soil by ammonia after treatment with dilute acid. The dark brown or black solution thus obtained contains large amounts of the phosphates and silicates of iron, aluminum and calcium, compounds which are not soluble in water or ammonia. Moreover, the ash ingredients of the solution cannot be detected by the ordinary reagents. In regard to this it may be said in the first place that the solution is not simply a solution of ammonia, but of humate of ammonium (using the term humate in a general sense), and it is well known that the presence of organic matter and of ammonium salts may have a very decided solvent action, and may prevent the precipitation of other substances without necessitating the assumption of a chemical union. Furthermore, Pitsch (*loc. cit.* 38) has found that humate of ammonium dissolves phosphates of calcium and iron, acting in this respect like ammonium citrate, and that from the solution so obtained the phosphoric acid can be precipitated by magnesia mixture if a large excess of the latter be used, just as is the case with the ammonium citrate solution. Moreover, in his diffusion experiments Grandeau found that the mineral matters of the *matière noir* passed through the membrane into the water outside it, where, so far as can be judged by the account given, they remained dissolved. If these mineral matters could thus remain dissolved in water containing, according to Grandeau, no trace of organic matter, it seems hardly necessary to assume that they were previously combined with the organic matter in order to explain their solubility in a solution of humate of ammonium.

It was hardly to be expected that a solution of ammonia should not remove some mineral matters from the soil. The preliminary treatment with acids must set free more or less silica from the hydrous silicates of the soil, which would then dissolve in the ammonia; though Grandeau makes the somewhat remarkable statement that the ammonia does not attack the silica of the soil, and gives this as one of his reasons for preferring it to a fixed alkali. The humate of ammonium, as we have seen, acts as a solvent of the more finely divided portions of the phosphates of the soil, while the presence of potash, soda, etc., in the extract is easily accounted for by an exchange of bases with the hydrous silicates just as in other cases of soil absorption. That the quantity

of mineral matter thus extracted should furnish a better indication of the fertility of the soil than the amount extracted by strong mineral acids might have been safely prophesied beforehand, but the facts afford no proof of the existence of any peculiar compound in the soil.

Attention has already been called to the fact that clay soils have shown the least agreement with the theory. Now these are exactly the soils which contain the largest proportion of hydrous silicates and insoluble phosphates, and show the greatest absorptive power. That is, they usually contain comparatively large amounts of plant food in a form insoluble in water, but, as we have reason to believe, readily attacked by the roots of plants, and also readily dissolved by dilute acids, but in combinations from which it would not be likely to be extracted very freely by ammonia or humate of ammonium. It is thus quite natural that the preliminary treatment with acid should rob these soils of a considerable portion of their available plant food, as in Pitsch's experiments, and that the amount extracted by ammonia should not measure as accurately the amount of available matters as in the case of a sandy soil, for example.

Grandeau also brings forward in support of his views the vegetation experiments with the Russian "black earth" in its natural state and deprived of its *matière noir*, and with soils to which organic matter had been added which have already been described. In the first of these experiments he claims that the fact that the bean refused to grow in the extracted soil is proof that the *matière noir* is indispensable. This, however, is begging the question. What the experiment really shows is that the treatment with acid and alkali removed almost all the available plant food. Whether all or any of it existed in the soil in combination with the organic matter, or whether if the latter alone could have been removed the fertility of the soil would have been affected, the experiment does not show.

Equally defective are the conclusions drawn from the experiments in which sterile peat was added to two soils, in that its effect on the physical properties of the soils is ignored. That peat is a useful amendment on many soils has long been known; that along with its physical effects it acts to increase the supply of available plant food is also true; but while Grandeau's results do not negative his theory, neither do they sustain it.

In short, Grandeau's experiments do not prove his theory, because they admit of other and, as it seems to the writer, simpler and more probable explanations.

The belief of practical agriculturists in the value of organic matter in the soil needs no such theory to reconcile it with the well established fact that the food of vegetation is mineral matter.

We divide the total plant food in the soil into two portions; one, and a comparatively small one, exists either actually in solution or

in a comparatively soluble form, and is the active portion of the soil; the other, and by far the larger, portion is simply rock fragments of various sizes, and is not immediately available to the plant. Every little fragment, however, is constantly subject to the same "weathering" which goes on in the larger masses, and under the influence of changes of temperature, frost, and the solvent action of water and saline solutions, is gradually rendered available to the plant. If by any means the amount of organic matter in the soil be increased, as in Grandeau's experiments for example, especially if it be finely divided and uniformly distributed, we have, as experiment has shown, a considerable increase in the carbonic acid of the soil, and hence an increase in the rapidity of the solvent action which converts rock dust into available plant food. Add to this the solvent action of the acids formed by the decay of organic matter, and the effect on the porosity, temperature, permeability, etc., of the soil, each in its turn reacting on the rate of weathering as well as on the growth of the crop, and we can readily see why "humus" should have a high value in the soil. We can see why a soil like the Russian black earth, where every mineral particle has its adjacent organic particle continually furnishing matter to dissolve it, should be a much more abundant source of plant food than a soil equally rich in minerals but lacking the organic matter.

Finally, the natural organic matter of the soil is a consequence as well as a cause of fertility. A large amount of humus in a soil implies an abundant previous growth of vegetation, and this in its turn implies a soil of at least moderate original fertility.

It is Grandeau's merit to have called attention emphatically to the value of the organic matter of the soil, and to have brought students of agricultural science to recollect, what they knew before, that the mineral matters of the soil are not the sole elements that determine its agricultural value; but his theory of the peculiar nature and functions of the *matière noir* seems to be one of those exaggerations into which it seems to be a law of nature that every one shall fall who sees clearly and presents forcibly and effectively any single aspect of a subject.

H. P. Armsby.

The Manufacture of Steel and Ingot Iron from Phosphoric Pig Iron.

A paper on this subject, by Sidney G. Thomas and Percy C. Gilchrist, was recently read before the Society of Arts, London. As it contains some new and interesting information in regard to an important application of chemistry, an abstract is here given:

"In America the deposits of Bessemer ore are very large, but are greatly exceeded in magnitude by the great phosphoric ore

tracts of Pennsylvania, Alabama, Tennessee and Virginia, and it is highly probable that the centre of the steel manufacture of the United States will on this account gradually gravitate southward. The fact that when iron ores are smelted in a blast furnace the whole of the phosphorus they contain will pass into the pig iron produced is too well known to require insisting upon. The only exception is in the case of a few small furnaces which, while producing a particular quantity of iron, will, when working on certain highly phosphoric ores, allow a trifling quantity of phosphoric acid to escape unreduced with the slag, though still producing a highly phosphoric pig iron. Nor does it seem at all probable that in the blast furnace, which is pre-eminently and necessarily a reducing, as opposed to an oxidizing apparatus, there is the slightest chance that the conditions can ever be so altered as to allow of any appreciable removal of phosphorus taking place in the manufacture of pig iron. The attempts that have been made to purify the ore before its introduction into the blast furnace—of which the only partially practicable one is Jacobi's—have also hitherto entirely failed of commercial success. The average proportion of phosphorus in our best known varieties of pig iron may be taken roughly to be as follows: Cleveland, 1.5 per cent.; Scotch, about 1 per cent ; Lincolnshire, 1.25 per cent.; Staffordshire cinder pig, 2.5 per cent.; Staffordshire mine pig, from .5 to 1 per cent.; Northamptonshire, 1.5 per cent. and over. It will thus be seen how far removed all these varieties of pig iron are from the non-dephosphorizing steel-maker's type, which, as we shall see, must not contain appreciably more than one-tenth of 1 per cent., or one part in 1000 of phosphorus.

"The fact that, till the year 1878, in neither of the two great steel-making processes, the Bessemer and Siemens, was phosphorus in the slightest degree removed, is also a matter of universal knowledge. In puddling, on the other hand, it has long been known that from 80 to 90 per cent. of the phosphorus present in the pig iron could be removed without difficulty. Thus, Cleveland pig iron containing 1.5 per cent. of phosphorus will make a puddled bar containing little more than 1-10th of this amount. We should not forget, however, that there is a third great system of steel making—the crucible-steel manufacture, based on the cementation process. As this, however, starts with iron which has already been dephosphorized and decarburized by the puddling or some analogous process, it may be disregarded for the present purpose, with the remark that no better material for the manufacture of cement or crucible steel could be obtained than the highly purified material which it will be shown can be so readily produced by the new Bessemer process. The proportions of the several kinds of steel manufactured in 1880 are estimated by the able Belgian metallurgist and statistician, M. Trasenster, to be as follows: Bessemer, 81 per cent.; Siemens, 16 per cent.; crucible,

nearly 4 per cent. It has been said that the presence of more than one part of phosphorus in 1000 of steel is fatal to good quality. This, too, needs some explanation and qualification. Steel may be roughly divided into three classes: hard steels, rail or medium steels, and soft steels. In hard steels containing ½ per cent. of carbon and more, the presence of as much phosphorus as above mentioned is highly prejudicial, rendering the material absolutely unfit for the manufacture of all the better class of tools. In rail steels one part in 1000 is considered in England quite as much as should be tolerated, though when the carbon is as low as ¼ per cent. half as much again may be carried with safety. In fact, in America the average home-made rails do not contain less than 1½ part of phosphorus per 1000. Many of the Continental rail steels also contain 1½ per 1000 of phosphorus and more; this being rendered comparatively safe by the fact that foreign engineers prefer rails with a lower content of carbon than is admitted in England.

"The Terrenoire Company and others, taking advantage of the fact that phosphorus is less dangerous in proportion as the amount of carbon in the rails is less, have, indeed, produced rails with 2-1000ths of phosphorus and very low carbon, which in ordinary climates are fairly reliable. For the soft steel and ingot iron containing less than 2-1000ths of carbon, which is now so largely used for manufactures other than rails, such as plates, wire, angles, rivets, sheets, and general purposes, it is also extremely desirable to keep the phosphorus lower than 1 per 1000. For good quality of boiler plates and other special purposes, half this amount should be considered as a maximum. Indeed, it may be taken as a rule that the lower the phosphorus the higher the quality. It is thus seen that in admitting 1-10th of 1 per cent. of phosphorus as the average maximum allowable for good steel, we have, if anything, given a high limit. It is now possible to appreciate more exactly the grounds for the statement that at least 85 to 90 per cent. of the iron ores of Great Britain, and probably nearly the same proportion of the whole known ore deposits of the world, are unavailable for steel-making without a practicable process of dephosphorization. In order to grasp more fully what this means, it may be well to examine into what forms the crude iron which is usually produced is transformed before it passes into consumption. For this purpose, M. Trasenter's figures may be again quoted. Assuming the world's production of pig iron to be 19,700,000 metric tons, approximately 5,250,000 tons are consumed in the manufacture of steel, 9,000,000 tons in the manufacture of iron, and 5,500,000 tons in the production of castings. Again, taking Mr. Jeans' carefully prepared figures for Great Britain, it appears that of the 8,370,000 tons of pig iron made in England, about 2,000,000 tons were employed in the manufacture of steel, and nearly 3,000,000 tons in the manufacture of puddled iron.

Now we have it on the excellent authority of Mr. Edward Williams, the late president of the Iron and Steel Institute, an iron and steel maker of wide and varied experience, that the consumption of coal in manufacturing steel rails from pig iron was, over a series of years, only a trifle over one-third of that employed in the manufacture of iron rails, while the wages cost for manufacturing steel rails is only 28 per cent. of that necessary for the manufacture of iron rails.[1]

"While there is no doubt that the economy of fuel and labor in the manufacture of steel as compared with that of iron is more conspicuous in the case of rail-making than in most other departments of manufacture, the figures above quoted may be taken as closely approximating to the truth in all cases, as, while puddling has, comparatively speaking, stood still for the past ten years, economy in steel-making has made, and is making, rapid progress. How then does it happen that there are 9,000,000 tons of pig iron annually turned into the unquestionably inferior material known as puddled iron, while only 5,500,000 tons are converted into the superior form of steel or ingot iron, particularly when so great an economy of fuel and labor could have been effected by turning the whole into the higher class material? May it not be fairly contended that it is really nothing but the absence of a practical and economical system of dephosphorization that could justify the existence of such an anomaly? It is now proposed to show that there is no reason for its continuance, since the developments and modifications introduced during the last four years enable steel of any desired purity as regards freedom not only from phosphorus, but from silicon and sulphur, to be produced readily and economically from the most highly phosphoric kinds of pig iron.

"The Bessemer process, with concurrent dephosphorization, as now regularly practiced at the Eston Works of Bolckow, Vaughan & Co. (who, under the able guidance of Mr. Windsor Richards, have been the pioneers of the new industry) and 13 other works in France, Belgium, Germany, Austria and Russia, is carried out as follows: The Bessemer vessel is lined with magnesian lime which has been previously subjected to an intense white heat, and so brought to a condition of density, tenacity and hardness as far as possible removed from the condition of the material generally known as well-burnt lime, and more closely resembling granite or flint. This material, which for brevity is known as 'shrunk lime' (as in course of preparation it shrinks to one-half the bulk of ordinary lime) is used either in the form of bricks or in admixture with tar as a rammed or slurry lining, this being substituted for the ordinary silica brick or silicious ganister lining of the hematite process. Before the metal (which may be either employed direct from the blast furnace without intervening remelting, or, if for any reason this is not convenient, may have been remelted in a cupola)

[1] Journal of the Iron and Steel Institute, p. 435.

is run into the converter, from 15 to 18 per cent. of its weight of common well-burnt lime is thrown into the vessel. The metal is then introduced and the charge is blown in the ordinary way to the point at which the ordinary Bessemer operation is stopped—that is, till the disappearance of the carbon, as indicated by the drop of the flame. The dephosphorizing process requires, however, to be continued for a further 100 to 300 seconds, this period of so-called after-blow, which would be prejudicial both to quality and yield in the ordinary process, being with phosphoric iron, under conditions permitting of the removal of phosphorus, that in which the great bulk of the phosphorus—down, indeed, to its last traces—is removed. The termination of the operation is shown by a peculiar change in the flame, and checked by a sample of the metal being rapidly taken from the turned-down converter, flattened under the hammer, quenched and broken, so as to indicate by its fracture whether the purification is complete. A practiced eye can immediately tell whether or no this is the case. If the metal requires further purification, this is effected by a few seconds' further blowing. The operation is thus, as will be seen, but little different from the ordinary Bessemer process. The differences that have been indicated, viz. the lime lining, the lime addition and the after-blow, are, however, sufficient not only to enable the whole of the phosphorus, which would be otherwise untouched, to be completely removed, but the silicon, of which inconvenient and even dangerous quantities are occasionally left in the regular Bessemer process, is also entirely eliminated, while at least 60 per cent. of any sulphur, also untouched in the ordinary process, which may have been present in the pig, is also expelled. It is found, too, that the once-dreaded phosphorus is of most substantial assistance in securing, by its combustion, the intense heat necessary for obtaining a successful blow and hot metal. If it is desired to produce ingot iron, or a metal differing only from puddled iron by its homogeneity and solidity, the usual recarburizing addition of spiegel is omitted or replaced by ½ per cent. of rich ferromanganese, which represents a considerable economy as compared with the cost of the spiegel necessary for the manufacture of harder steel. The phosphorus is oxidized by the blast, forming phosphoric acid, which, finding itself in presence of two strong bases, oxide of iron and lime, unites with the latter of them to form phosphate of lime, which passes into the slag. Whether or no there is a transitory formation of phosphate of lime, making oxide of iron perform the function of a carrier, is a matter, though interesting theoretically, which it is needless here to discuss.

"The order of the removal of the several impurities is well indicated by the diagrams on the wall, for which we are indebted to M. Meier, of Luxembourg, and M. Massenez, of Hoerde. It will here be seen that in the first stage of the operation phosphorus is the substance which is least attacked, while, as the blow advances,

and particularly after decarburization, its removal becomes more and more rapid. The contrast between the two operations, it will be observed by reference to diagram 5 (representing an ordinary hematite blow, examined by Mr. Snelus), is most noticeable in the phosphorus curves. In the one, the proportion of this element slightly but distinctly increases from the commencement to the end of the operation. In the other the removal, at first slow, becomes eventually rapid, till ultimately it is entirely at the discretion of the operator whether more than one part in 5000 shall remain. As an instance of the purity of the metal that can be at will produced from pig iron, such as is ordinarily made in Scotland, Staffordshire and Lincolnshire, we may quote analyses made so long ago as the spring of 1880, at Seraing, of steel made at Wittkowitz by the basic process:

	Sil.	Car.	Sul.	Phos.	Man.
Plate No. 1[1]	.000	.04	.01	.008	.29
Plate No. 2	.000	.09	.01	.014	.20
Square bar	.000	.06	.01	.011	.26
Round bar	.000	.07	.01	.000	.26

"It will be seen that these bear comparison with even the phenomenally pure Bessemer steel of Sweden, of which the following is an average anaylsis as given by Akerman:

Sil.	Car.	Sul.	Phos.	Man.
.017[2]	.1	trace	.028	.15
to	to	to	to	to
.029	.3	.01	.031	.36

"The basic Siemens and Siemens-Martin processes are carried out on the same lines as the Bessemer process. The dephosphorization is very complete, but the operation takes about 5 per cent. longer time than when pure material is used; the proportion of lime required is less than in the Bessemer process, and the wear of the basic hearth, with suitable arrangements, is not excessive. The limits of time and your patience render it necessary, for the present, to postpone the detailed consideration of this very interesting and important branch of the subject of dephosphorization, and to confine our attention to the Bessemer process, in which, moreover, most experience has been gained, though many thousand of tons of dephosphorized Siemens steel have been produced, and the process is regularly worked in Continental works.

"It cannot be too clearly understood that among the chief features of the dephosphorizing Bessemer process are, first, its controllability, and secondly, its peculiar suitability for the manufacture of soft steel or ingot iron. Its controllability appears especially to depend upon the fact that while any phosphorus remains it apparently exercises a protective influence on the iron, and so to

[1] Journal of the Iron and Steel Institute, 1880, 115. [2] *Ibid.*

prevent the tendency to red-shortness, which demands so much skill to avoid in the regular Bessemer process, when soft steel is aimed at. On these points we cannot do better than quote the opinion of Mr. Walrand, who has a long experience of both processes at the great steel works of Creusot. Mr. Walrand expresses himself as follows: 'Those who are occupied in the manufacture of Bessemer steel know how difficult it is to obtain with regularity the extra soft steel employed for boilers in the French navy. Such metal appeared only to be made in the Martin furnace, and even then it was necessary to employ picked material in its manufacture. But by the new Bessemer dephosphorizing process, steels of an extraordinary degree of softness can be obtained with the greatest facility, and at a price less than that of ordinary rail steel. By treating a pig containing from 1.5 to 2 per cent. of manganese, we obtain, after the decarbonization and dephosphorization is finished, a non-oxidized metal which does not contain more than traces of carbon or manganese. If it be desired that the steel should be entirely free from any tendency to red-shortness, we may add from 0.25 to 0.50 per cent. of a rich ferromanganese to remove any traces of oxygenization. The only precaution to be taken to obtain a soft steel is to choose pig (if direct working be employed) which contains sufficient manganese, with 2 per cent. as a maximum, or to make a suitable mixture of pigs, if cupolas be employed. But this will be by no means the only outlet for dephosphorized metal, for up to the present time the high price of soft steel has been the great obstacle which has prevented many people from employing it in construction. But by the new process soft metal can be produced at a less price than ordinary (puddled) iron. There is, therefore, no longer any reason, apart from routine, why steel should not be employed in all cases in place of iron, to which it is so much superior in strength.'

"Having endeavored to show that there are strong reasons why the manufacture of puddled iron should be superseded by a process which is not only highly economical, but which produces an ingot or homogeneous product of superior strength, ductility and elasticity, it may be useful to summarize what is being done in the way of manufacturing and preparing for the manufacture of dephosphorized steel. In England, Bolckow, Vaughan & Co. are making weekly about 2300 tons of Cleveland steel, while on the Continent there are 13 works, producing an aggregate of about 7000 tons a week of dephosphorized Bessemer and Siemens steel. The total make is, therefore, at the rate of over 450,000 tons a year. In England there are six converters building for the process, which will probably produce about 3500 tons a week.

"On the Continent there are 25 converters building for the process, with a minimum capacity of 9000 tons a week. Now, as the make of pig iron in England far exceeds that of the whole Continent of Europe, it is clear that we are in this matter allowing our Continental friends to push ahead of us in a way that Englishmen

have not hitherto been accustomed to. Whether in this we are wise it is left for others to decide; but one thing is clear, that in all neutral markets our puddled iron will have to contend in future with Continental dephosphorized ingot iron, which can be sold at a lower price and will stand far higher tests. Whether the prediction of Von Tunner (the father of scientific iron manufacture) that the extinction of puddling works is, by the increase of the production of ingot iron by the dephosphorizing method, imminent, is to be proximately realized or not we shall soon have an opportunity of knowing. Lest any apprehension should be felt as to the outlet which is to be found for so much ingot iron, it may be called to mind that we made last year nearly 2,700,000 tons of puddled iron, and imported 90,000 tons in addition. The saving in coal alone, had this been made by an ingot process, would have amounted to nearly 2,000,000 tons, while the smaller worth in converting ingot iron to finished iron would have saved nearly £700,000 worth of material."

NOTES.

Transmission of Gases through Fluids of different Densities. A Lecture Experiment.

If in a given acidified and nearly saturated solution of a salt (I have generally used ferrous sulphate and added a small quantity of sulphuric acid) a piece of zinc is placed, and this solution carefully overlaid with common water, the bubbles of hydrogen appear to meet with considerable resistance at the zone of contact between the two liquids, and from one-third to one-half are reflected downward and to one side. Finally, however, they are again induced by their relative levity to rise; and now scattered, and at a part of the vessel remote from their first ascent, pass through the upper zone and escape into the air.

This phenomenon is again exhibited if upon the second or upper stratum a third liquid is superimposed having a density less than that of water. The appearances at this second zone are however not quite as marked as at the first.

What is the cause of this apparent reflection of the hydrogen bubbles in passing from a denser into a rarer medium? I confess that at present a wholly satisfactory explanation does not occur to me.

Certainly it does not appear reasonable that the circumstance of their meeting with less resistance on entering the rarer medium should occasion a reflection, though by virtue of the reduced dif-

ference between the densities of the aeriform body in this second stratum and its enveloping fluid it is conceivable why, perhaps, a less rapid upward movement should result. Is not, however, this influence in favor of a less rapid movement more than compensated for by the diminished resistance of this second medium? Be this as it may, it still cannot explain, I think, why there is a positive reflection of a large part of the bubbles. It might explain a mere retarding in their movement.

In explanation of the above phenomenon it may also be assumed that the bubbles of gas as they rise from the saline liquid into the water above carry with them their envelope, *i. e.* the thin film of solution encircling them. When, therefore, they enter the upper liquid they are too much weighted down to pass at once through the latter, and are therefore detained for an instant. In the meanwhile they are caught by the descending current of the solution, and are for a time carried sidewards and downwards. This downward current is caused as a result of the upward current formed by the rapid ascent of the hydrogen set free by the zinc. I am devising experiments to settle this, if possible, and hope soon to report.

C. GILBERT WHEELER.

Separation of Gallium.

M. LECOQ DE BOISBAUDRAN gives some processes for the quantitative analysis of salts of gallium and the separation of gallium from other metals.

1. *Separation from the alkalies (Cs, Rb, K, Na, Li, and NH_4).* When the proportion of gallium is not very small, the simplest method consists in adding an excess of ammonia to the hydrochloric acid solution and boiling the mixture, adding water from time to time to supply the loss by evaporation, until a piece of litmus paper, previously placed in the liquid, becomes distinctly red. The precipitated oxide of gallium is then filtered off, washed, dried and ignited.

In case there be but a small trace of gallium in the mixture, the boiling solution is treated with cupric hydroxide. The mixture of Ga_2O_3 and copper oxide is then dissolved in excess of hydrochloric acid, the copper removed by sulphuretted hydrogen, and the gallium then precipitated by ammonia as above.

Separation from the alkaline earths (Ba, Sr, and Ca).—If the gallium is in considerable quantity, it can be precipitated directly by the addition of excess of ammonia, followed by long-continued boiling, the oxides of the alkaline earths remaining in solution.

Traces of gallium are separated from large amounts of Ba, Sr, or Ca by means of copper hydroxide, or the greater part of the Sr and Ca and all the Ba may be first removed from the solution by the addition of sulphuric acid and alcohol; if this be done the gallium oxide must be strongly ignited, in order to drive off all the sulphuric acid.

Separation from magnesium.—Prolonged boiling with excess of ammonia answers well. The process with copper hydroxide may be employed in the case of small quantities of gallium mixed with large amounts of magnesium.

Separation from alumina and chromic oxide.—The most convenient process consists in precipitating the gallium by means of potassium ferrocyanide, from a hydrochloric acid solution containing at least a quarter or a third of its volume of concentrated HCl.

When the gallium is present only in very small quantity (less than $\frac{1}{1000}$), one or two days are necessary for its complete precipitation. The precipitate is then filtered off, dried by a gentle heat and ignited; there results a mixture of the oxides of gallium and iron, which can be separated by a method which M. Lecoq de Boisbaudran promises to give shortly. The almost inevitable formation of a little Prussian blue in the strongly acid solution is of no importance, as it only has the effect of slightly increasing the proportion of ferric oxide to be afterwards separated from the oxide of gallium.—(*Comptes Rendus*, **94**, 1227.)

R. D. C.

On the Use of Liquefied Gas, and in particular of Ethylene, for the Production of Low Temperatures.

L. CAILLETET gives an account of some of his experiments on the use of liquefied gas, particularly ethylene, for the production of low temperatures.

Ethylene is liquefied at $+1°$ by a pressure of 45 atmospheres; its critical point is in the neighborhood of $+13°$, while that of carbon dioxide corresponds to $+31°$. These properties led Cailletet to determine whether a more intense cold could not be produced by liquefied ethylene than by liquefied nitrous oxide. In order to compare these temperatures, he made use of a thermometer with an arbitrary scale, filled with carbon bisulphide. When plunged in liquefied ethylene this thermometer indicated a temperature corresponding closely to $-105°$, far below that caused by liquid nitrous oxide, which is $-88°$.

The ethylene used in the experiments was prepared in the usual way by heating a mixture of alcohol and concentrated sulphuric acid, and after being purified by passing through cold sulphuric acid and caustic potash solution, to remove the ether and sulphur dioxide, was compressed by means of a powerful pump, designed by M. Cailletet, in bottles previously tested by a pressure of several hundred atmospheres. By this apparatus, ethylene was readily liquefied, but its employment in the liquid state presented serious difficulties, for when the attempt was made to draw off the liquid ethylene from the bottle in the ordinary way, as with nitrous oxide, no trace of liquid was obtained, and it was there-

fore necessary to devise a special apparatus in order to make use of it as a source of cold.

When liquid ethylene is allowed to escape from the receiver in such a manner that the liquid drops strike directly against the apparatus to be cooled, there is no great loss of the liquid, and the temperature is further lowered by the expansion of the gas not liquefied. These conditions are best realized by fixing the receiver containing the cooled liquid ethylene in an iron support, and attaching to the orifice of the receiver, directed downwards, a tube of glass of 5 or 6 mm. diameter, bent at a right angle. When the stop-cock is opened the compressed gas and the liquid are projected with moderate velocity against the apparatus to be cooled. Liquefied ethylene, by evaporation at the atmospheric pressure, can then produce a cold more intense than has hitherto been realized by any other means; it possesses the advantage, moreover, of remaining liquid and transparent at temperatures at which nitrous oxide and carbon dioxide become solid and opaque.

In experimenting upon the liquefaction of oxygen with the aid of liquid ethylene, M. Cailletet has obtained interesting results differing entirely from those previously observed by him when nitrous oxide was made use of as a source of cold. In the latter case, when the tension of the compressed oxygen, cooled to —88° by means of liquid nitrous oxide, was suddenly diminished by allowing a portion of it to escape, there was produced a light cloud which disappeared immediately on stopping the escape of the gas; when, however, the oxygen was cooled to at least —105° by means of liquid ethylene, there was noticed an appearance of tumultuous ebullition which lasted for quite an appreciable time, and which resembled the sudden projection of a liquid into the tube.

M. Cailletet hopes to produce still lower temperatures by condensing, by means of the apparatus now at his disposal, gases more difficultly liquefiable than ethelyne.—(*Comptes Rendus*, **94**, 1224).

R. D. C.

On the Liquefaction of Ozone.

MM. P. HAUTEFEUILLE and J. CHAPPUIS have experimented upon the liquefaction of ozone, using for the purpose the apparatus of M. Cailletet mentioned in the preceding note.

A study of the conditions under which a sudden diminution of the tension of a compressed mixture of oxygen determined the formation of a cloud, led them to the conclusion that pure ozone would be little more difficultly liquefiable than carbon dioxide, and they found that the addition of carbon dioxide to the mixture of the gases yielded by compression a liquid colored pale blue, which coloration they attributed to ozone liquefied at the same time with

the carbon dioxide. From these facts they concluded that it was possible to obtain ozone in the liquid form, and that the liquid would be strongly colored. Their conclusions have been fully confirmed by experiment, and they have obtained ozone in liquid drops of a deep indigo blue color; this liquid, they state, was preserved for more than 30 minutes under a pressure of 75 atmospheres, its evaporation not being very rapid even under the atmospheric pressure.

The liquefaction was accomplished by compressing to about 125 atmospheres a mixture of ozone and oxygen in the receiver of the apparatus of M. Cailletet. To this receiver was attached an upright capillary tube, the upper part of which was curved back upon itself so that the descending branch could be exposed to a jet of liquid ethylene, by which means it was cooled to a temperature probably below —100°.

On experimenting with a gas containing not more than 10 per cent. by weight of ozone, the gas compressed to 125 atmospheres was not appreciably colored in the ascending branch of the tube, while in the cooled portion the blue coloration was very decided. Upon allowing a portion of the gas to escape suddenly the tube instantly became colorless, and in the drawn-out portion at the end there was formed a drop of deep indigo blue colored liquid; the ozone in the tube being almost totally condensed there, as a further compression to 150 atmospheres did not give an appreciable color to the cooled tube. Once liquefied, ozone will preserve this state for a considerable time in a capillary tube, even at the atmospheric pressure, and can be examined either in the jet of liquid ethylene or by withdrawing the tube from it for a short time. The deep blue liquid diminishes little by little in volume, its vaporization being so slow and its diffusion so rapid that the gas appears colorless above an almost black liquid, and it is only at the moment that the last traces of the liquid disappear that it can be seen that an azure blue gas is produced. The vaporization of the liquid ozone brings the whole apparatus back to its initial state provided the ozone has not been slowly decomposed by the mercury used in compressing the gas.—(*Comptes Rendus*, **94**, 1249.)

R. D. C.

On Anhydrous Crystallized Grape-Sugar from Solutions in Water.

Crystallized anhydrous glucose has hitherto been obtained only from alcoholic solutions. ARNO BEHR has recently found that glucose can, under certain conditions, be obtained as the anhydride in crystallized form from solutions in water. This result may be accomplished by putting some crystallized anhydrous glucose in a concentrated aqueous solution of glucose. A good concentration for the purpose is a solution containing 12 to 15 per cent. of water. A temperature of from 30 to 35° C. is apparently

the best. The author found, further, that the addition of crystals of anhydrous glucose is not necessary. In fairly pure concentrated solutions of glucose at somewhat elevated temperatures, the crystallization of the anhydride is the normal result. In order, however, to effect a crystallization as uniform as possible, it is advisable to add a little of the dry crystalline powder, though only a very little is necessary. The crystallization of anhydrous glucose is similar to that of cane sugar. The syrup leaves the crystals easily under the influence of centrifugal force. The sweetness of glucose is to that of cane sugar about as 1 to $1\frac{9}{13}$.—(*Berichte der deutsch. chem. Gesell.* **15,** 1104.)

The Atomic Weight of Uranium.

CLEMENS ZIMMERMAN[1] has prepared metallic uranium by Peligot's method, and determined some of its properties. Its sp. gr. is 18.685, and its sp. heat between 99° and 0° is .02765. The latter number multiplied by 240 gives a product of 6.64, which agrees with the mean atomic heat indicated by Dulong and Petit's law. The controversy between the values 120, 180 and 240 for the atomic weight of uranium is thus settled in favor of the highest, and in accordance with Mendelejeff's classification.

F. W. C.

[1] Ber. d. deutsch. chem. Gesell. **15,** 847.